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Part I. A New Synthesis of Dihydrojasmone. Part II. Dehydration Studies of Some Cycloalkanols.

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Part I. A NEW SYNTHESIS OF DIHYDROJASMONE
Part II. DEHYDRATION STUDIES OF SOME CYCLOALKANOLS

A Dissertation

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by
Ronald Joseph Allain
B.S., Louisiana State University, 1963
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He is grateful to his wife, Janet, for the encouragement and kind understanding.

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ABSTRACT

Part I. Dihydrojasmone (3-methyl-2-amylcyclopent-2-en-1-one) was prepared from levulinic acid, a readily available compound obtained from wood. Dihydrojasmone is an important ordorous substance in the perfume industry.

The method of preparation of dihydrojasmone involved seven steps. The ethyl ester of levulinic acid was prepared in the usual way and then the keto group of ethyl levulinate was protected by conversion to the ethylene ketal. This ethylene ketal was reacted with methylsulfinyl carbanion, $CH_3SOCH_2^-$ (prepared from dimethyl sulfoxide and sodium hydride) to give the β-ketosulfoxide, $CH_3CCH_2CH_2CCH_2SCH_3$. The alkylation of this β-ketosulfoxide was accomplished in dimethyl sulfoxide as solvent, with sodium hydride and amyl bromide. This alkylated β-ketosulfoxide was not isolated, but reduced with aluminum amalgam to 2,5-undecanedione-2-ethylene ketal, which after treatment with dilute sulfuric acid gave 2,5-undecanedione. This γ-diketone was cyclized with dilute sodium hydroxide solution to the desired product, dihydrojasmone.

Part II. A study was made of the products of dehydration of some tertiary alcohols of cyclooctane and cyclododecyl derivatives.

The following alcohols were prepared by the reaction of cyclooctanone or cyclododecanone with the appropriate Grignard reagent: 1-propylcyclooctanol, 1-butylcyclooctanol, 1-amylcyclooctanol, 1-allylcyclooctanol, 1-benzylcyclooctanol, 1-propylcyclododecanol, 1-butylcyclododecanol, 1-amylcyclododecanol, 1-allylcyclododecanol, and 1-benzylcyclododecanol. The alcohols were identified from the infrared spectra and by preparing a phenyl urethan as a solid derivative.

The alcohols were dehydrated by refluxing with phosphoric acid. 1-Propylcycloctanol gave 88% 1-propyl-cis-cyclooctene and 12% propylidenecyclooctane; 1-butylcyclooctanol gave 91.4% 1-butyl-cis-cyclooctene and 8.6% butylidenecyclooctane; 1-amylcyclooctanol gave 90.7% 1-amyl-cis-cyclooctene and 9.3% amylidenecyclooctane; 1-allylcyclooctanol gave 92.5% 1-allyl-cis-cyclooctene and 7.5% allylidenecyclooctane; 1-benzylcyclooctanol gave 100% 1-benzyl-cis-cyclooctene; 1-propylcyclododecanol gave 33% 1-propyl-cis-cyclododecene and 67% 1-propyl-trans-cyclododecene; 1-butylcyclododecanol gave 29.1% 1-butyl-cis-cyclododecene and 70.9% 1-butyl-trans-cyclododecene; 1-amylcyclododecanol gave 26.4% 1-amyl-cis-cyclododecene and 73.6% 1-amyl-trans-cyclododecene; 1-allylcyclododecanol gave 24.2% of 1-allyl-cis-cyclododcecene, 56.7% 1-allyl-trans-cyclododecene and 19.1% of three unidentified compounds; 1-benzylcyclododecanol gave 23% 1-benzyl-cis-cyclododecene and 77% 1-benzyl-trans-cyclododecene.

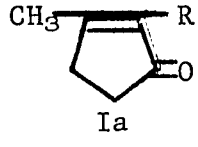
The products of the dehydrations were identified by the use of infrared spectra, nuclear magnetic resonance spectra and vapor phase chromatography.

Part I.

A New Synthesis of Dihydrojasmone

DISCUSSION

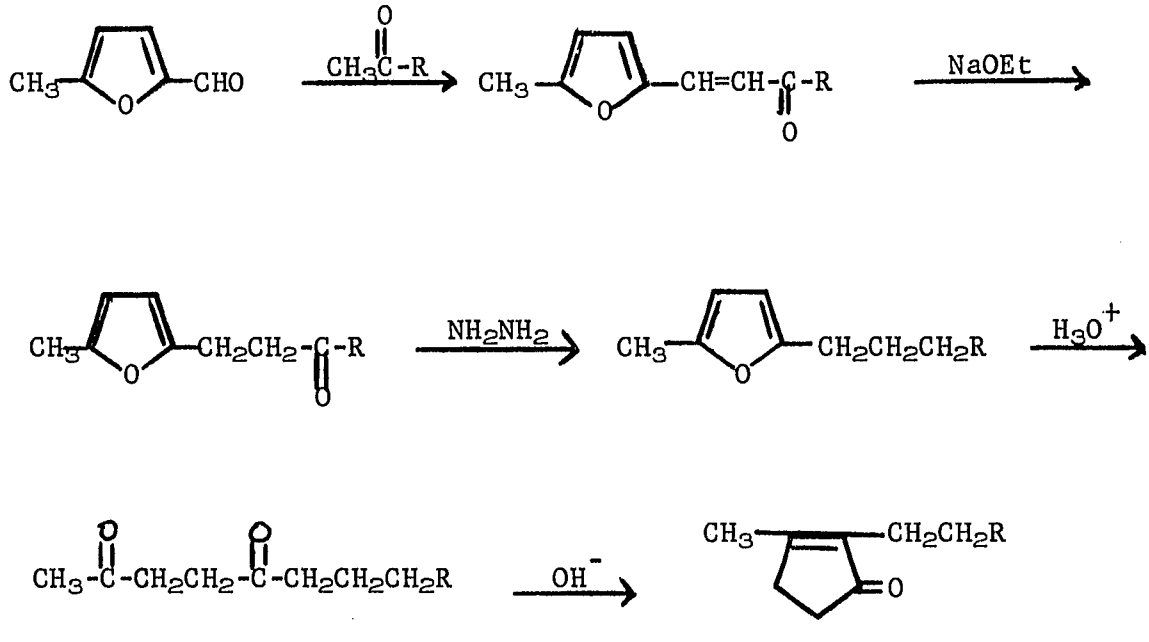
Cyclopentenones may be divided into two classes: 3-cyclopentenones and 2-cyclopentenones, which differ only in the position of the double bond. While numerous mono- and disbustituted 2-cyclopentenones are known, this investigation is limited to methods of synthesis of 3-methyl-2-alkylcyclopent-2-en-1-ones (Ia). This type is of unusual interest because a number of compounds of natural occurrence have closely related structures and are important odorous substances; e.g.



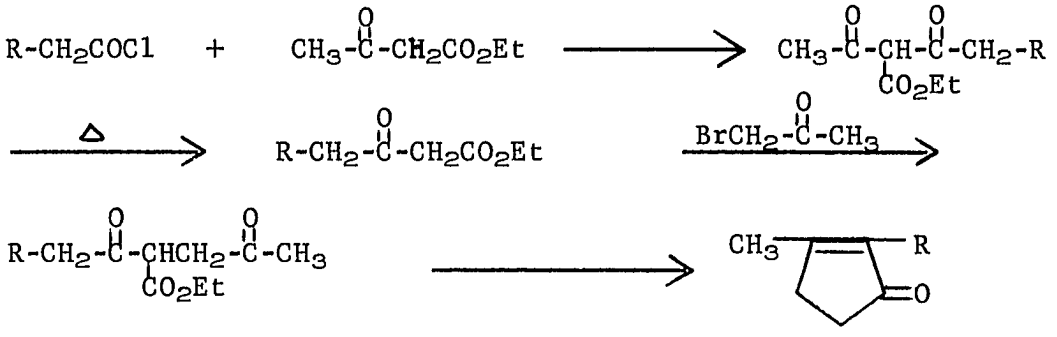
Ia

R	
$CH_3CH_2CH_2CH_2CH_2-$	Dihydrojasmone
$CH_3CH_2CH=CHCH_2-$	Jasmone
$CH_3CH=CHCH_2-$	Cinerone
$CH_3CH_2CH_2CH_2-$	Dihydrocinerone
$CH_2=CHCH=CHCH_2-$	Pyrethrone

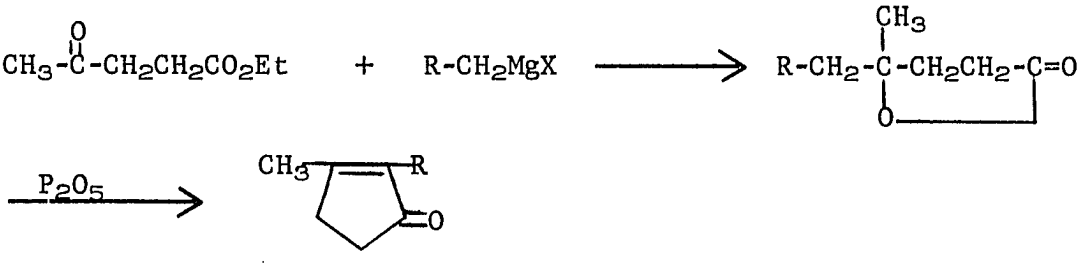
The synthesis of 3-methyl-2-alkylcyclopent-2-en-1-ones (Ia) have been accomplished in several ways. Hunsdiecker[1] prepared 1,4-alkanediones, starting with 5-methylfurfural, and has shown that they may be cyclized to give cyclopentenones of the type Ia.



Another method dependent upon the cyclization of 1,4-alkanediones is that of Crombie and co-workers[2] as shown by the following steps in the process:

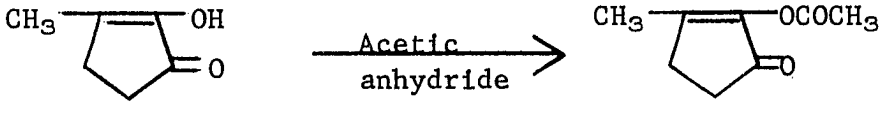


Frank and co-workers[3,4] were the first to prepare 3-methyl-2-alkylcyclopent-2-en-1-ones from γ-methyl- γ-alkyl- γ-butyrolactones. These lactones were obtained from ethyl levulinate and the appropriate Grignard reagent.

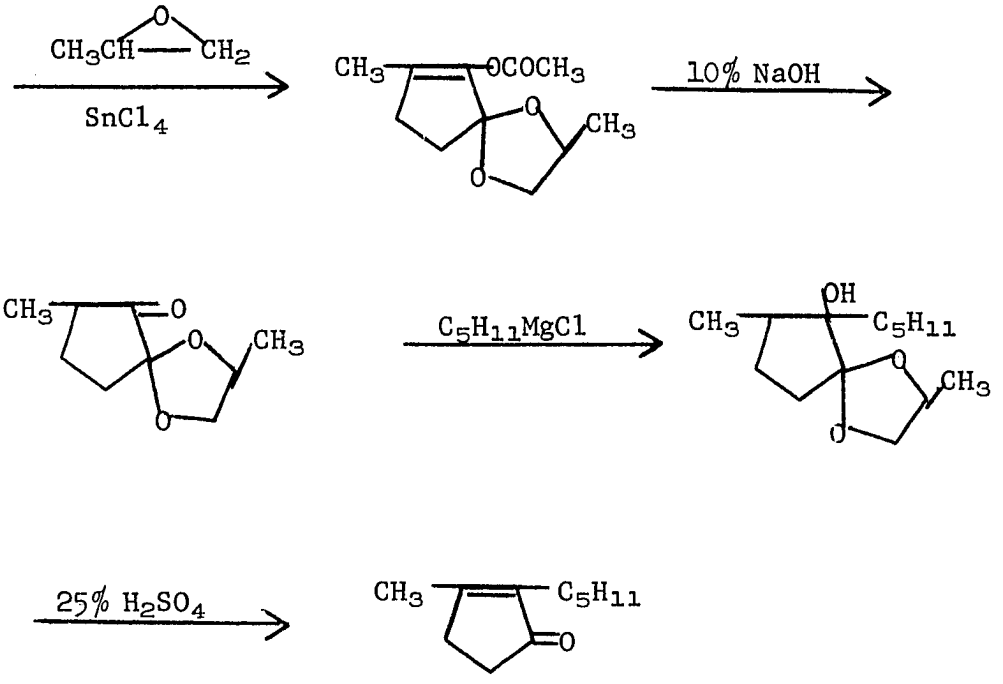


Other workers[5] have found that polyphosphoric acid is a better dehydrating agent in this case than phosphorous pentoxide.

All of the above methods require a cyclization step. Erickson and Collins[6] have synthesized dihydrojasmone and have avoided the cyclization step, by starting with a readily available cyclopentenone, 3-methylcyclopent-2-en-2-ol-1-one (III).

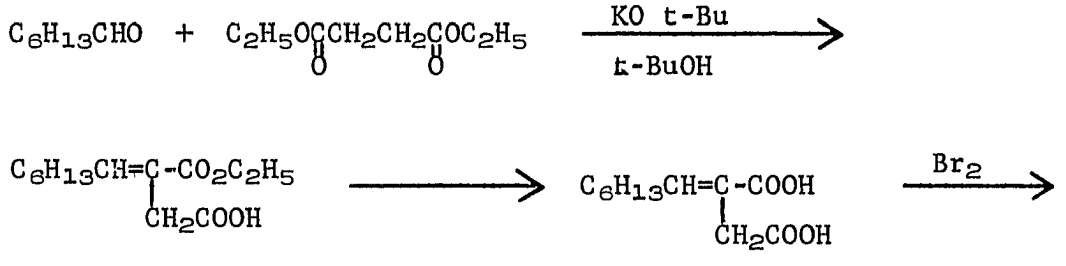


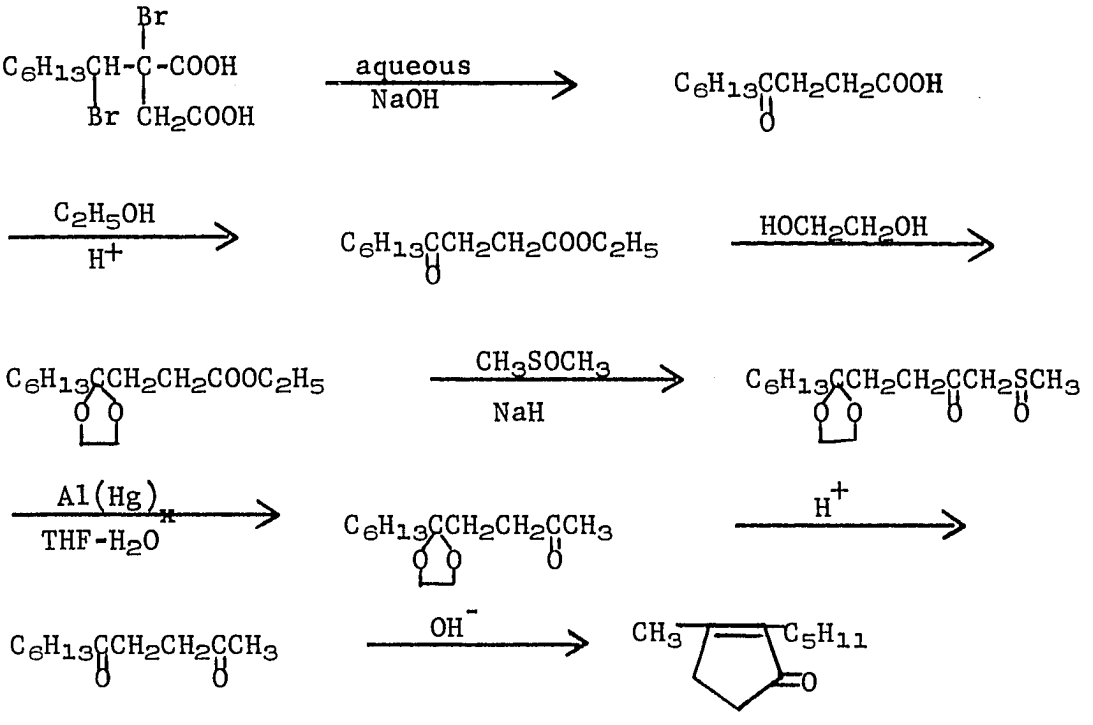
III



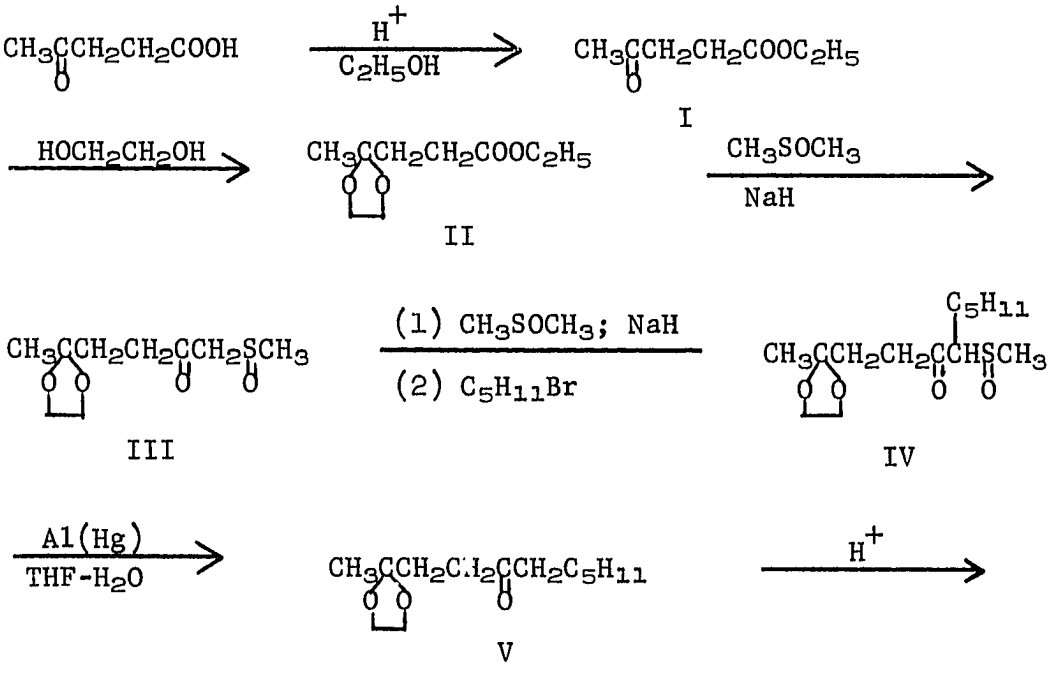
Other methods of preparing jasmone[7,8,9] and dihydrojasmone[10,11,12,13] have been reported.

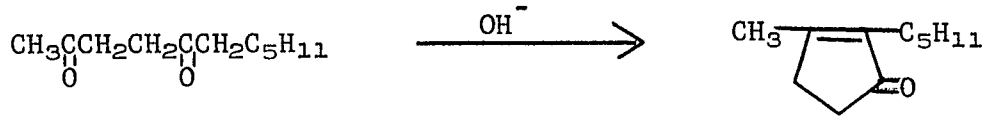
In the present investigation, the goal was to find a new and shorter method of synthesis of these cyclopentenones from readily available materials via the cyclization of 2,5-alkanediones to the corresponding 3-methyl-2-alkylcyclopent-2-en-1-ones (Ia). The Grignard reagent was avoided since it is not very feasible on a large industrial scale. Recently, while we were completing the synthesis, a group of Japanese workers[14] prepared dihydrojasmone by a similar method. However, we feel that our procedure has the advantage in that all our starting materials are readily available. These workers first prepared γ-ketodecanoic acid[15] as outlined below:





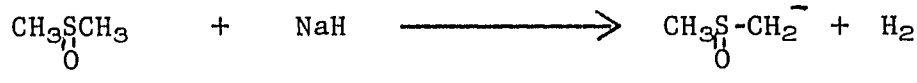
As shown, their synthesis involves ten separate steps, while the synthesis in our investigation reguired only seven steps. The starting material is the readily available keto acid, levulinic acid, which is a by-product in paper production from wood. The general scheme is outlined below:



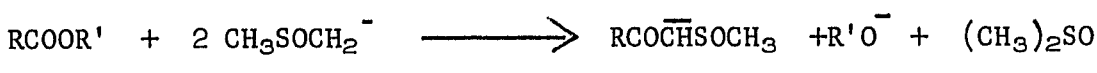


VI VII

The ester I and ketal II were prepared in the usual way. The preparation of the β-ketosulfoxide III from ketal II is based upon a method by Corey and Chaykovsky[16,17,18] and by Russell.[19,20] The methylsulfinyl carbanion involves the production of the conjugate base of dimethyl sulfoxide. This carbanion can be generated by heating powdered sodium hydride in an excess of dimethyl sulfoxide under a nitrogen atmosphere at 70-75°:

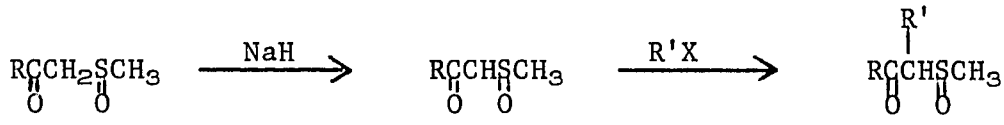


Esters which do not undergo facile proton transfer react with two equivalents of the methylsulfinyl carbanion to form anions of β-ketosulfoxides according to the equation:

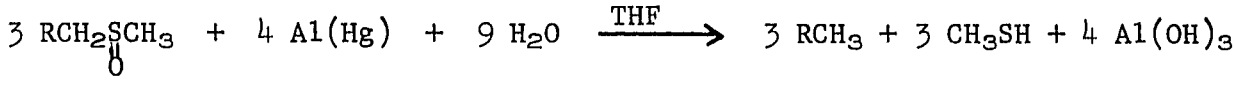


This accounts for the conversion of the ketal ester II to the ketal β-ketosulfoxide III.

The transformation of III ⟶ IV was carried out according to the method of Gassman and Richmond,[21] which involves the alkylation of a β-ketosulfoxide. This procedure is very similar to alkylation of β-diketones as in the classical acetoacetic ester synthesis of ketones, a synthesis generally limited to the synthesis of methyl ketones. Gassman and Richmond found that β-ketosulfoxides could be alkylated by the use of sodium hydride in dimethyl sulfoxide as solvent.

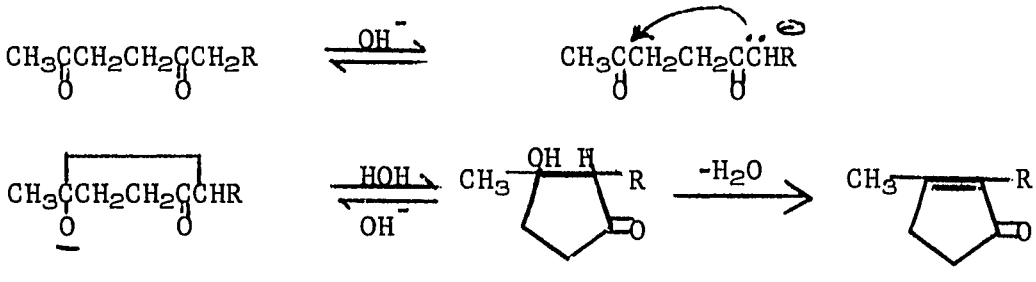


The crude β-ketosulfoxide was reduced to the ketal ketone V without purification. The reductive cleavage was carried out with aluminum amalgam in aqueous tetrahydrofuran according to the procedure of Corey and Chaykovsky:[18]



The removal of the ketal protective group (V ⟶ VI) was accomplished in the usual way with dilute acid.

One of the more interesting steps in the sequence is that of the cyclization of the diketone (VI) to the cyclopentenone (VII) that was first described by Hunsdiecker[1] in 1942. This step involves an intramolecular base-catalyzed aldo condensation followed by dehydration.



This synthesis can be adapted to prepare other substituted 5-methyl-2-alkylcyclopent-2-en-1-ones.

Experimental[22]

Levulinic acid and dimethyl sulfoxide were obtained from the Crown Zellerbach Corporation. The dimethyl sulfoxide was purified before use by distilling from calcium hydride; 64°/(4 mm); while the levulinic acid was used as received.

Ethyl levulinate (I). This was prepared according to the method of Frank.[3] Levulinic acid, 464 g. (4.0 moles), ethanol, 368 g. (8.0 moles), benzene, 400 ml. and sulfuric acid, 5 ml., were refluxed together under a Diens-Stark trap for 8 hours. After removal of most of the ethanol, the remaining organic portion was washed with water and then dried over potassium carbonate. The benzene was then removed by distillation and the residue vacuum distilled to give 532 g. of ethyl levulinate (92.0%); b.p. 84-85°/(10 mm); n_D^{20} 1.4228.

Ethyl levulinate ethylene ketal (II). A mixture of 144 g. (1.0 moles) ethyl levulinate, 74.4 g. (1.2 moles) ethylene glycol, 250 ml. of benzene and 1.0 g. p-toluenesulfonic acid were refluxed under a Diens-Stark trap for 10 hours. The mixture was washed sequentally with 20 ml. of water, 20 ml. of 10% sodium carbonate solution and subsequently dried over anhydrous sodium carbonate. The dried mixture was vacuum distilled to give 133.5 g. (71%) of a product with the properties: b.p. 104-105°/(10 mm), n_D^{20} 1.4335, and λ_{max} 3.35, 3.46, 5.73, 6.90, 7.26, 7.68, 7.95, 8.49, 8.80, 9.11, 9.48-9.58, 10.55, and 11.58 μ.

Anal. Calcd. for $C_9H_{16}O_4$: C,57.43; H,8.57. Found: C,57.73; H,8.75.

β-Ketosulfoxide of Ethyl levulinate ethylene ketal (III). This was prepared according to the method of Corey and Chaykovsky.[18] Two-tenths moles (9.6 g.) of sodium hydride (50% by weight in mineral oil dispersion) was placed in a four neck flask, fitted with stirrer,

reflux condenser, thermometer and dropping funnel. The sodium hydride was washed with petroleum ether, by swirling, allowing the sodium hydride to settle, and decanting the liquid in order to remove most of the mineral oil. The last trace of petroleum ether was removed by evacuating the system and immediately filling with dry nitrogen. Subsequently, 125 ml. of dry dimethyl sulfoxide was added and the mixture heated with stirring and the temperature maintained between 70-75° until evolution of hydrogen ceased. After cooling to room temperature, 125 ml. of tetrahydrofuran which had been dried over KOH and distilled from $LiAlH_4$ was added and the solution cooled in an ice bath during the slow addition of 18.8 g. (0.1 moles) of ethyl levulinate ethylene ketal (II). The ice bath was removed and the reaction mixture was stirred for thirty minutes. The mixture was then poured into 600 ml. of water and acidified with HCl to a pH of 3-4. This aqueous solution was extracted with six-50 ml. portions of chloroform. The combined chloroform extracts were washed with two-30 ml. portions of water and was then dried over anhydrous magnesium sulfate. After removal of the chloroform the yellow oily residue remaining (13.1 g.) was distilled to give 10.6 g. (48%) of a product having the following properties: b.p. 105-106°/(0.5 mm); $\lambda_{max}^{CCl_4}$ 3.35, 3.46, 5.78, 7.25, 8.80, 9.11, 9.48-9.58, and 11.55 μ.

Anal. Calcd for $C_9H_{16}O_4S$: C,49.08; H,7.32. Found: C,49.07; H,7.67.

2,5-Undecanedione-2-ethylene ketal (IV). The alkylation of III was carried out according to the method of Gassman and Richmond[21] and the subsequent reduction to IV with aluminum amalgam according to the method of Corey and Chaykovsky.[18] Methylsulfinyl carbanion was prepared as before from 4.8 g. (0.1 moles) of sodium hydride (50% by weight in mineral oil dispersion) and 67 ml. of dry dimethyl sulfoxide. To this solution of methylsulfinyl carbanion was added 22.0 g. (0.1 moles) of the β-ketosulfoxide (III) in 25 ml. of dimethyl sulfoxide. The temperature was kept at 20°. When evolution of hydrogen ceased, 15.1 g. (0.1 moles) of amyl bromide was added and the reaction mixture stirred for one hour at room temperature. The mixture was diluted with 250 ml. of water and extracted with five-50 ml. portions of chloroform. The combined portions of chloro-

form were dried over anhydrous magnesium sulfate. After removal of the chloroform under vacuum, 11.3 g. of an oily residue remained. No attempt was made to purify the residue. The crude alkylation product was dissolved in 675 m. of 10% aqueous tetrahydrofuran. This was placed in a two liter flask equipped with a stirrer and aluminum amalgam from 10.8 g. (0.4 g.-atm.) of aluminum was added. The aluminum amalgam was prepared by cutting aluminum foil into strips approximately 10 cm. x 1 cm. and immersed, all at once, into a 2% aqueous solution of mercuric chloride for 15 seconds. The amalgamated strips were rinsed with absolute alcohol and then with ether and cut immediately, and directly into the reaction vessel, into pieces approximately 1 cm. square. The stirred mixture was then heated at 65° for one hour after which time it was cooled and filtered. The filtered solids were washed with 50 ml. of tetrahydrofuran. After removal of most of the tetrahydrofuran by distillation, ether was added to the residue. The organic phase was separated and dried over anhydrous magnesium sulfate. The ether was removed and the residue was distilled to give 8.3 g. of compound IV: b.p. 114-115°/(2 mm); n_D^{20} 1.4660; λ_{max} 3.35, 3.46, 5.82, 7.26, 8.59, 8.73, 9.09, 9.43, and 11.56 μ.

Anal. Calcd. for $C_{13}H_{24}O_3$: C,68.38; H,10.59. Found: C,68.59; H10.50.

2,5-Undecanedione (VI). To 8.0 g. (0.035 moles) of the ketone ketal (IV(was added 50 ml. of 15% sulfuric acid solution. The resulting suspension was stirred and refluxed for two hours and then an additional 50 ml. of water was added and the mixture steam distilled. The organic layer was separated and the aqueous layer was saturated with sodium chloride before extraction with 100 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate. After removing the ether, the residue was distilled to give 5.2 g. (82%) of compound VI; b.p. 118-119°/(10 mm); (lit.[1] 141°/(14 mm)). This sample solidified upon standing; m.p. 33-34°; $\lambda_{max}^{CCl_4}$ 2.93, 3.38,

3.43, 5.85, 6.12, 7.10, 7.30, 7.64, 8.11, 8.61, 9.30, 9.62, and 10.32 μ.

Anal. Calcd. for $C_{11}H_{20}O_2$: C,71.69; H,10.94. Found: C,71.83; H,10.81.

Dihydrojasmone (VII). 2,5-Undecanedione was cyclized to dihydrojasmone according to the method of Hunsdiecker.[1] To 5.0 g. (0.027 moles) of 2,5-undecanedione (VI), 75 ml. of 2% sodium hydroxide solution and 25 ml. of ethanol were added and the mixture refluxed for six hours. After cooling, the organic layer was taken up in 100 ml. of ether and dried over anhydrous sodium sulfate. The ether was removed and the residue distilled to give 4.0 g. (90%) of dihydrojasmone: b.p. 86-87°/(2 mm); n_D^{20} 1.4790; λ_{max} 3.43, 5.85, 6.05, 6.93, 7.09, 7.23, 7.40, 7.48, 7.72, 8.50, and 9.93 μ.

Anal. Calcd for $C_{11}H_{18}O$: C,79.46; H,10.91. Found: C,79.70; H,11.12.

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Part II.

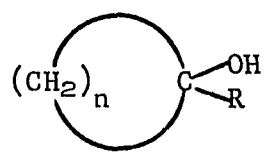
Dehydration Studies of some Cycloalkanols

INTRODUCTION

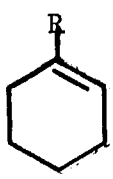
Nearly all olefin-forming elimination reactions of any theoretical or synthetic importance are β-eliminations, in which two groups are lost from adjacent carbon atoms:

One of the more important reactions of this type is the dehydration of alcohols. This affords an efficient synthesis of many alkenes, which would otherwise be very difficult to obtain.

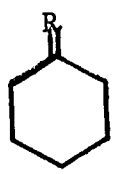
It has long been recognized that the tendency of an alcohol to dehydrate was closely related to the spatial arrangement of the various groups. Of special interest is the dehydration of cyclic alcohols, since from the analysis of the products formed, one can gain an insight into the strain that exists in the ring system under consideration. The alcohols which are to be studied and discussed are of the general type:



Zelinski and Namjetkin[1] synthesized 1-methylcyclopentanol but did not subject it to dehydration studies. Wallach[2] dehydrated some 1-alkylcyclohexanols with sulfuric acid as catalyst and by oxidation of the olefins showed them to have structure I instead of structure II.



I



II

Signaigo and Cramer[3] also studied the dehydration of these substituted cyclohexanols and by analogy to Wallach's results assigned structure I to the resulting alkenes. These alcohols were dehydrated by distillation from anhydrous aluminum sulfate. Mosher[4] also made a study of the dehydration of 1-alkylcyclohexanols. 1-Methyl-, 1-ethyl-, and 1-isopropylcyclohexanol were dehydrated by heating with iodine. The location of the double bond in the alkene formed upon dehydration was proved by ozonolysis. The following endo:exo percentages were found: 100:0 for methyl; 99:1 for ethyl; and 95:5 for isopropyl.

McLellan and Edwards[5] prepared and fully characterized a series of 1-alkylcyclopentanols where the alkyl groups were: methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, decyl, dodecyl, and tetradecyl. The dehydration of these alcohols was not studied by these authors. Crane, Boord and Henne[6] dehydrated some 1-alkylcyclopentanols to the corresponding alkenes but they did not study the composition of the alkenes, since the alkenes were then hydrogenated to the saturated system. Williams and Edwards[7] prepared six 1-n,alkylcyclohexanols with alkyl groups: ethyl, butyl, hexyl, heptyl, octyl, and dodecyl. However these authors did not study the dehydration of the alcohols. Fieser and Szmuszlovicz[8] prepared aromatic derivatives of cyclopentyl, cyclohexyl, and cyclooctyl tertiary alcohols and subjected them to dehydration; but here, since R is aromatic, only the endo product is formed. Woodward and McLellan[9] studied the dehydration of a series of 1-n,alkylcyclopentanols, with the alkyl groups ranging from methyl to hexyl. In all cases the only product found by ozonolysis was the isomer with the double bond in the ring. The relative efficiencies of eleven catalysts upon the dehydration of 1-ethylcyclopentanol were also studied. The catalysts investigated were: (a) vapor phase: aluminum phosphate, aluminum oxide, and barium oxide; (b) liquid phase: phosphoric acid, sulfuric acid, oxalic acid (solid and in solution), potassium bisulfate, iodine, zinc chloride, and barium oxide. In method (a), aluminum oxide was found to be the most efficient

and in method (b), phosphoric acid was the best. The position of the double bond was not affected by the various catalysts employed.

Schmidt and Gemassmer[10] also studied the dehydration of 1-n, alkylcyclopentanols, but not as in detail. They, too, reported that the product of dehydration was the isomer in which the double bond was within the ring. Harris and McLellan[11] studied the 1-alkenylcyclopentanol series. The substituted groups were: vinyl, allyl, 3-butenyl, and 4-pentenyl. Dehydration studies of 1-allylcyclopentanol, using three different catalysts, gave in all cases, 1-allylcyclopent-1-ene. Dennissenko[12] dehydrated 1-benzylcyclopentanol, but made no effort to locate the double bond in the alkene formed upon dehydration. 1-(4-Pentenyl)-cyclopentanol was dehydrated by Marvel and Brooks,[13] but no attempt was made to establish the position of the double bond. Leach and McLellan,[14] using phosphoric acid as catalyst, dehydrated 1-benzylcyclopentanol which yielded 70.1% benzylidenecyclopentane and 29.9% 1-benzylcyclopentene. Dehydration of 1-isopropylcyclopentanol yielded 97% isopropylidenecyclopentane and 3% 1-isoproylcyclopentene. 1-Vinylcyclopentanol yielded 100% 1-vinylcyclopentene. Plate and Melinikov[15] performed dehydration studies on some cyclopentanols with the use of oxalic acid. They reported that 1-ethylycyclopentanol gave a 7:1 ratio of 1-ethylcyclopentene to ethylidenecyclopentane; 1-propylcyclopentanol gave a 7:1 ratio of 1-propylcyclopentene to propylidenecyclopentane; and 1-butylcyclopentanol gave a 7:1 ratio of 1-butylcyclopentene to butylidenecyclopentane.

Traynelis and co-workers[16,17] have studied the dehydration of alcohols in dimethyl sulfoxide. Among the alcohols studied were the 1-alkylcycloalkanols. Analysis of the olefin composition was by v.p.c. while identification of these products employed various combinations of physical constants, infrared spectra and/or n.m.r. spectra. The results are shown in Table I. Gelli[18] and his co-workers have also studied the dehydration of alcohols in dimethyl sulfoxide. They

studied the dehydration of $(CH_2)_n(OH)Y$ and fcund the results as shown in Table II. Hofmann[19] and his workers have discussed the mechanism of β-elimination reactions in dimethyl sulfoxide.

Table I

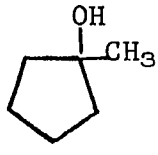
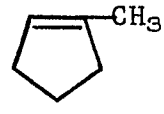
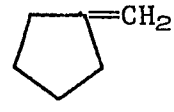
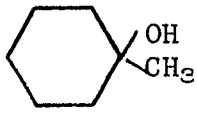
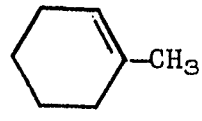
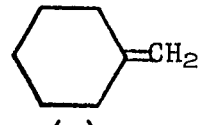
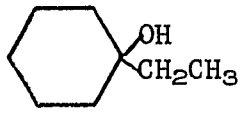
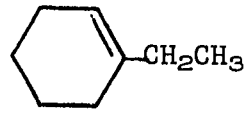
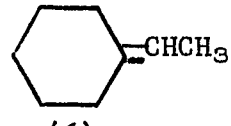
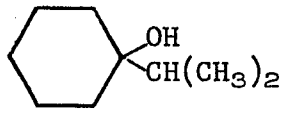
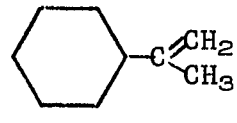
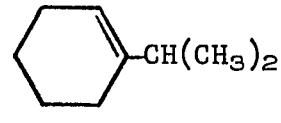
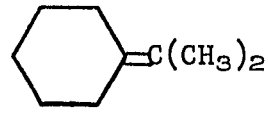
Alcohol	Olein Yield, %	Olein Composition
	88	 (100)  (0)
	74.5	 (95)  (5)
	55.5	 (94)  (6)
	62	 (5.4)  (78.3)  (16.3)

Table II

n	Y	%yield	% endo	% exo
4	Methyl	85	100	0
5	Methyl	78	95	5
6	Methyl	70	55	45
4	Ethyl	80	68	32
5	Ethyl	60	94	6
6	Ethyl	63	65	35

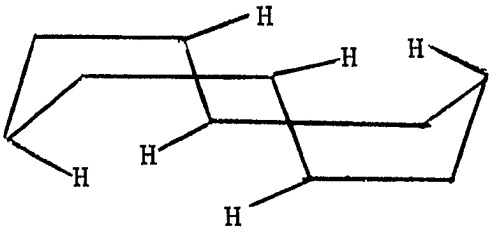
Herling,[20] et. al. have performed the acid catalyzed dehydration of the appropriate tertiary alcohol and have reported the following compositions of alkenes: 98% 1-methylcyclopentene and 2% exo product; 92% 1-ethylcyclopentene and 8% exo product; and 89% 1-ethylcyclohexene and 11% exo product.

Cope and Van Orden[21] reacted cyclooctanone and butylmagnesium bromide but made no attempt to isolate the resulting alcohol. The crude oil was treated with iodine and distilled to give a product, described as 1-butylcyclooctene. However, the authors stated, "the position of the double bond was not proved and the product may be a mixture rather than a single isomer." This product was then hydrogenated to give butylcycloctane. Brown and Borkowski[22] prepared 1-methylcyclooctanol and dehydrated it to 1-methylcyclooctene.

From this reveiw of the literature it was found that the dehydration of the cyclopentyl and cyclohexyl alcohols have been studied in considerable detail. Cycloheptyl and cyclooctyl alcohols have been studied to a much lesser extent, and the cyclododecyl system has not been studied.

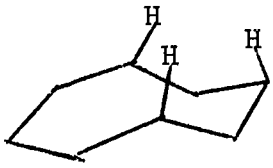
DISCUSSION AND RESULTS

The cyclooctyl and cyclododecyl systems were studied because of the abnormal reactions of the medium rings. Cyclic compounds of eight- to twelve-members are known as medium rings. Synthetic difficulties, certain anomalous physical properties and abnormal transannular reactions are usually attributed to compression in the interior of the ring.[23] Torsional (Pitzer) strain, due to lateral repulsion between vicinal groups and angular (Baeyer) strain accounts for some of this strain, but strong intra-annular repulsions by end-on interaction of hydrogen atoms pointing into the ring appears to be the major factor in this strain. X-ray data[24] have shown the transannular hydrogen-hydrogen atomic distances to be less than van der Waals radii. The Dunitz[24] conformation for cyclodecane (III) has six such transannular hydrogen repulsions.

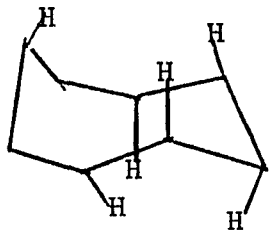


III

Hendrickson[25] in a very elegant paper has described a system for defining all the possbile symmetrical medium-ring cycloalkane conformations. Calculations of the minimum-energy form of each of these symmetrical cycloalkanes are presented. The results imply two conformations (IV and V) for cyclooctane are most favorable.

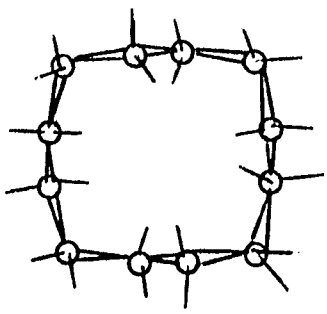


IV

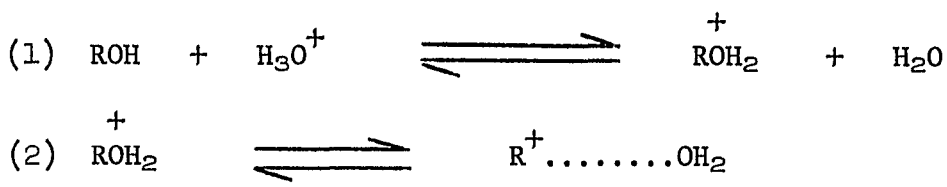


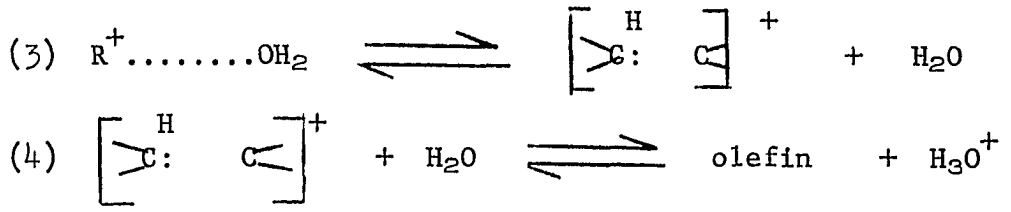
V

For cyclododecane,[26] a variety of molecular models without angle strain (Baeyer strain) can be constructed, yet the real molecule[27] is beleived to be so shaped as to avoid as much torsional strain (Pitzer strain) as possible, all bonds being roughly staggered with acceptance of some angle strain by openeing of certain C-C-C angles (from 109° to 117°).



The acid-catalyzed dehydration of alcohols appears to involve carbonium ion intermediates. Taft and his co-workers[28,29] have proposed a mechanism for this dehydration. On the basis of results obtained from O^{18} exchange rates, inductive effects, entropies of activation, effects of ring size on dehydration and equilibrium, dependence of rates of olefin hydration on acidity and on ring size, and leaving group effect on substitution-elimination rates, the following mechanism was proposed for olefin-alcohol interconversion.





Step (3) is the rate determining step. The transition state is represented by a structure possessing a triple character, that is, a hybrid with some of the properties of an olefin, a conjugate acid of an alcohol, and a carbonium ion.

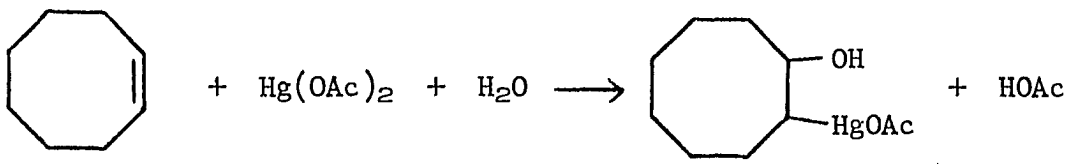
In this mechanism, factors that tend to stablize a carbonium ion would tend to cause the dehydration to proceed at a faster rate. Thus if the cyclic compound is more stable with an sp^2-hybridized carbon atom (a carbonium ion in this case) than with an sp^3-hybridized carbon atom in the ring, then the dehydration rate will be enhanced. Some data have been obtained for cyclic compounds for the transitions $sp^2 \longrightarrow sp^3$ and $sp^3 \longrightarrow sp^2$ by Brown.[30,31] These data show that the rate of reduction of medium-ring ketones ($sp^2 \longrightarrow sp^3$) is considerably slower than that of cyclohexanone or acyclic ketones (column A). For the solvolysis of cycloalkyl tosylates ($sp^3 \longrightarrow sp^2$), the rate is greatly enhanced for medium-ring compounds (column B). These data indicate that the sp^2-hybridized carbon atom is appreciably stablized relative to an sp^3-hybridized carbon atom for medium-sized rings. These results are shown in Table III.

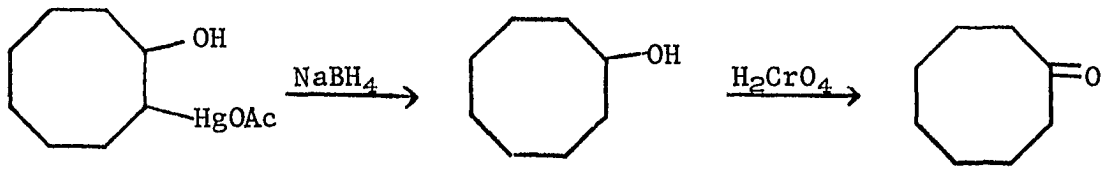
Table III

Ring Size	A	B
Acyclic	1.00	1.00
6	355	0.75
8	0.17	144
9	0.07	129
10	0.03	286
11	0.05	31
12	0.40	2.4

From this table, it can be seen also that the 12-membered ring approaches the reactivity of the acyclic system.

All of the tertiary alcohols in this study were prepared by the reaction of cyclooctanone or cyclododecanone with the appropriate Grignard reagent. Some of the cyclooctanone and cyclododecanone used was prepared by oxymercuration[32,33,34] of the corresponding olefin combined with the reduction of the oxymercurial intermediate by sodium borohydride.[35] The resulting crude alcohol was oxidized with chromic acid.[36] This method has previously been used for the preparation of cyclooctanone, but not for cyclododecanone. The reaction sequence is shown below for cyclooctene.





The addition is first order in mercuric salt, first order in olefin and is stereospecific.[32]

The conversion of cyclododecanone to the tertiary alcohols via the Grignard reaction proceeded smoothly with yields in the neighborhood of 56-77%. However, in the reaction of cyclooctanone, the addition of the ketone to the solution of the Grignard reagent was accompanied by evolution of a gas, (except in the case of the amyl and benzyl Grignard reagents). This gas was presumably propane,

butane, or propene, depending on the Grignard reagent used. The gas is ascribed to the enolization of the ketone.[16] Cope and Fenton[37] recovered considerable quantities of cyclooctanone from the reaction product of the ketone and ethylmagnesium iodide and also ascribed the result to ready enolization of the cyclic ketone. Craig and Larrabee[38] noted also that 1-ethylcyclooctanol behaves similarily and undergoes dehydration upon attempted distillation. Gero[39] has studied the enol contents of the cycloalkanones and found the results shown in Table IV.

Table IV

Ketone	% enol
cyclobutanone	0.55
cyclopentanone	0.09
cyclohexanone	1.18
cycloheptanone	0.17
cyclooctanone	9.3
cyclononanone	4.0
cyclodecanone	6.1

These ketones were dissolved in 70% aqueous methanol. The enol content of a ketone was determined by adding excess iodine monochloride to a mixture of the ketone with dry sodium bicarbonate, adding excess sodium iodide solution and titrating with thiosulfate solution.

As can be seen from Table IV, cyclooctanone has the highest enol content. According to Gero, a model of the enol of cyclooctanone demonstrates that except for the coplanar group, all C and H atoms are more or less in skew position and one H at C-5 is close enough to the enolic double bond to represent something like a transannular pi-complex as shown in VII. The extremely high enol content

VII

of cyclooctanone is noteworthy; the carbonyl group of this ketone is very unreactive. Cyclooctanone forms no bisulfite addition product. In the Stuart model of cyclooctanone the carbonyl group does not appear to be more hindered than that of cyclohexanone, but repulsive interactions may force the molecule to assume more hindered conformations.

Thus, along with each cyclooctyl alcohol, a small amount of cyclooctanone (about 10%) was present. In order to remove this impurity, the product mixture from the Grignard reaction was reacted with the Grignard reagent again, thereby reducing the amount of cyclooctanone present in the mixture to about 3-4%. This procedure was repeated until less than 1% of cyclooctanone was present in the cyclooctyl alcohols as shown by the infrared spectra.

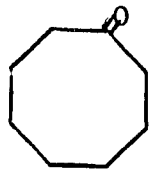
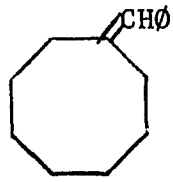
All of the alcohols were dehydrated by heating with phosphoric acid, and the resulting mixture was analyzed by the use of infrared spectra, nuclear magnetic resonance and vapor phase chromatography.

Attempts were made to prepare the pure exocyclic olefin by two procedures. The first method attempted was the Wittig reaction. Gelli[40] and his workers have prepared ethylidendcyclopentane, -cyclo hexane, and -cycloheptane by this method. Attempts to prepare benzylidenecyclooctane (as shown by the sequence below) failed.

(1) $\phi_3P + \phi CH_2Cl$

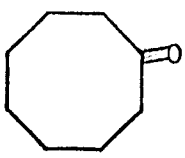
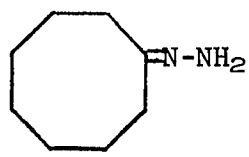
(1) $\phi_3P + \phi CH_2Cl \longrightarrow [\phi_3\overset{+}{P}CH_2\phi]Cl^-$

(2) $[\phi_3\overset{+}{P}CH_2\phi]Cl^- \xrightarrow{\text{n-BuLi}} \phi_3P{=}CH\phi \longleftrightarrow \phi_3\overset{+}{P}{-}\overset{-}{C}H\phi$

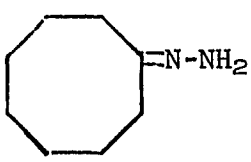
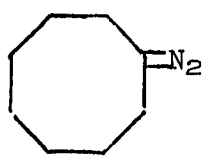
(3) $\phi_3P{=}CH\phi \longleftrightarrow \overset{+}{\phi_3P}\text{-}\overset{-}{CH}\phi$ +  → 

+ $\phi_3P{\rightarrow}O$

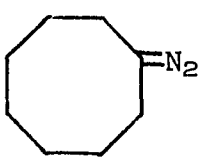
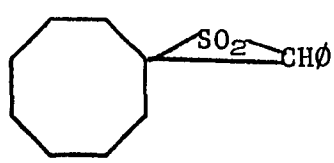
The second method attempted was via the reaction of a diazo compound with a sulfene,[42] as outlined in the reaction sequence below.

(1)  $\xrightarrow{NH_2NH_2.H_2O}$ 

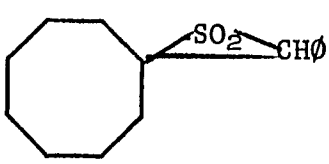
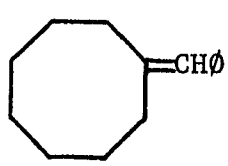
VIII

(2)  $\xrightarrow[BaO]{Ag_2O}$ 

VIII IX

(3)  $\xrightarrow[Et_3N]{\phi CH_2SO_2Cl}$ 

IX X

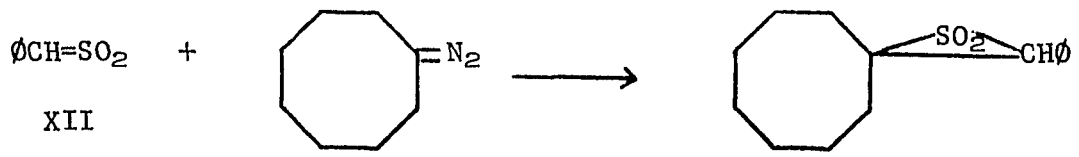
(4)  $\xrightarrow{-SO_2}$ 

X XI

The diazo compound (IX) was prepared from the hydrazone (VIII) as shown in steps (1) and (2) according to the procedure of Heyns and Heins.[41] These authors prepared diazocyclohexane in similar fashion. In step (3) the diazo compound was reacted with the sulfene, produced by the elimination of HCl from benzylsulfonyl chloride[43] as shown below:

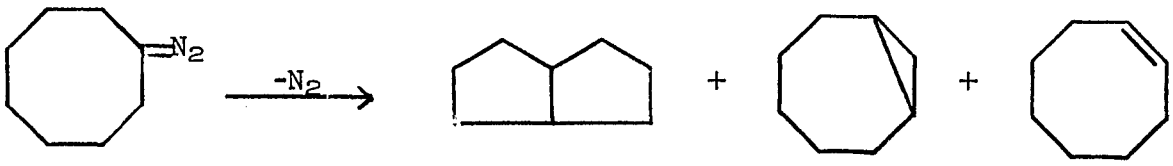
$$\phi CH_2SO_2Cl + (C_2H_5)_3N \longrightarrow \underset{\text{XII}}{\phi CH{=}SO_2} + \left[(C_2H_5)_3\overset{+}{N}H\right]Cl^-$$

The sulfene (XII) reacts with the diazo compound (IX) to give a three-membered ring sulfone (X).[44,45]



IX X

This sulfone, upon heating, loses SO_2 to give the desired exo olefin.[44,45] However, attempts to prepare XI by this method failed. The diazo compound was formed as evidence by the deep red color of the solution. But in order for reaction (3) to take place, the temperature had to be about -5°. At this temperature, decomposition of the diazo compound occured before the reaction with the sulfene could take place. The only product that could be isolated was cyclooctene. In contrast to this result, Friedman and Shechter[46] report that the decomposition of diazocyclooctane, generated by decomposition of the tosylhydrazone with sodium methoxide in diethyl Carbitol, gave products other than cyclooctene.



46% 9% 45%

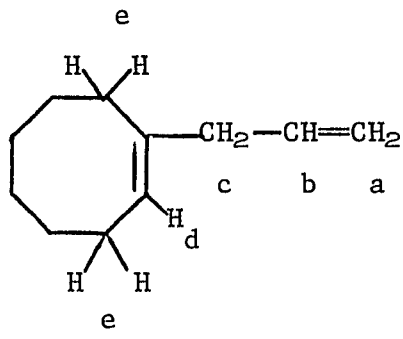
All of the alcohols were dehydrated by heating the alcohol with a small amount of phosphoric acid. The cyclooctyl alcohols dehydrated more readily than did the cyclododecyl alcohols. All of the cyclooctyl alcohols were completely dehydrated (as evidenced by the absence of the hydroxyl stretching vibrations in the infrared spectrum) in slightly less than thirty minutes. The cyclododecyl alcohols were completely dehydrated in about one hour. The explanation for this observation is relief of transannular strain in the cyclooctyl system. This strain is not present in the cyclododecyl system.

1-Propylcyclooctanol was dehydrated to give 88% of 1-propyl-cis-cyclooctene and 12% of propylidenecyclooctane; 1-butylcyclooctanol gave 91.4% 1-butyl-cis-cyclooctene and 8.6% butylidenecyclooctane; and 1-amylcyclooctanol gave 90.7% of 1-amyl-cis-cyclooctene and 9.3% of amylidenecyclooctane. The percentage of these products was determined by vapor phase chromatography on a Carbowax column. In each case, only two products were observed. No trans-cyclooctenes were formed as evidenced by the absence of an absorption in the region of 10.3-10.42 μ of the infrared spectrum. An absorption in this region is caused by the out-of-plane bending vibration for olefinic C-H of a trans-compound. Absorptions at 11.41 μ indicate a cis-configuration. A bicyclic product was ruled out on the basis of the 100 mc n.m.r. spectrum. In all cases the vinyl proton signal was a broadened triplet at 5.31δ J=8 cps for the cis compound and a small broad signal at 5.12δ which was assigned to the vinyl proton in the exo-olefinic compound. The allylic protons appear as a multiplet at 1.99δ. These protons appear in a ratio of 1 (Vinyl):6

(allylic). The rest of the protons are also in the correct ratio. If a bicyclic compound were present the ratio of the vinyl protons to the alkyl protons would not be correct. There is no 1-alkyl-trans-cyclooctene as shown by the infrared spectrum and also by the n.m.r. spectrum. If the trans-isomer were present this vinyl proton would be in a different chemical environment than in the cis-isomer and thus would have a different chemical shift, and two sets of triplets would be observed instead of one.

It was noted that cyclooctanol when dehydrated also gives similar results. M. Godchot[47] and E. P. Kohler[48] investigated the acid-catalyzed dehydration of cyclooctanol and obtained a cyclooctene of refractive index 1.4693. R. Willstatter and E. Waser,[49] however, had reported a refractive index of 1.4739, for material obtained by pyrolysis of cyclooctyltrimethylammonium hydroxide. Ziegler[50] confirmed both observations and showed that the isomers are, respectively, cis- and trans-cyclooctene.

The dehydration of 1-allylcyclooctanol gave 92.5% 1-allyl-cis-cyclooctene and 7.5% allylidenecyclooctane. Analysis of the mixture by v.p.c. showed the presence of only two compounds having retention times of 17.2 minutes (92.5%) and 28.8 minutes (7.5%). This indicates quite a difference in polarity of the compounds and suggests that the latter compound may have conjugated double bonds. The infrared spectrum shows an absorption at 5.98 μ and a stronger one at 6.08 μ. The latter absorption is accorded to the terminal methylene, $=CH_2$, which is known to have a very strong absorption. A weak absorption appears at 6.24 μ, indicating the presence of small quantities of a conjugated double bond since this absorption band is usually intense. Strong bands appear at 10.06 μ and 11.00 μ for the out-of-plane bending vibrations for $-CH=CH_2$. There is also an absorption band at 11.42 μ indicating the cis-cyclooctene isomer. The n.m.r. spectrum confirms structure XIII as the major product.



XIII

A complex multiplet, centered at 5.71 δ, appears and is assigned to proton b. A broadened triplet appears at 5.32 δ (J = 8 cps) and is assigned to proton d. A complex multiplet centered at 4.95 δ appears and is assigned to protons a. A broadened multiplet appears at 2.12 δ and is assigned to allylic protons e. A broadened doublet appears at 2.69 δ (J = 8 cps) and is assigned to allylic protons c. The ratios of the protons are in agreement with the assigned structure. Since the minor product is only 7.5% of the total, this does not affect the n.m.r. spectrum significantly.

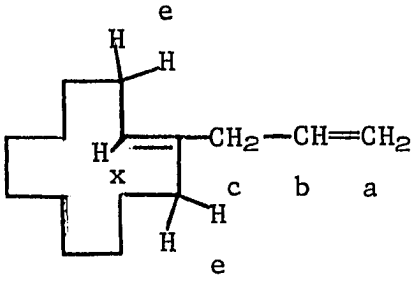
The dehydration of 1-benzylcyclooctanol gave 1-benzyl-cis-cyclooctene as the only product. V.p.c. analysis showed the presence of only one compound. The infrared spectrum showed an absorption band at 5.99 μ (C=C) and at 6.21 μ (aromatic C=C stretch). Conjugation of an olefinic double bond, with an aromatic ring, would result in enhanced olefinic absorption near 6.15 μ. In a conjugated system containing an aromatic C=C bond, a stretching absorption band occurs near 6.28 μ. The spectrum indicates no conjugation of the double bond with the aromatic ring..An absorption band occurs at 11.42 μ which is accorded to the cis =CH bending vibrations. The n.m.r. spectrum show a broadened triplet at 5.35 δ which is assigned to the vinyl proton; a singlet at 4.24 δ assigned to the two benzyl protons, and a multiplet at 3.07 δ assigned to the four allylic protons in the ring. The proton ratios are in agreement with the assigned structure.

The dehydration of 1-propylcyclododecanol gave 33% 1-propyl-cis-cyclododecene and 67% 1-propyl-trans-cyclododecene; 1-butyl-cyclododecanol gave 29.1% 1-butyl-cis-cyclododecene and 70.9% 1-butyl-trans-cyclododecene; and 1-amylcyclododecanol gave 26.4% 1-amyl-cis-cyclododecene and 73.6% 1-amyl-trans-cyclododecene.

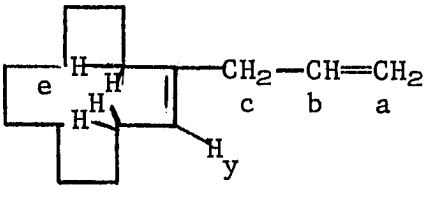
Various cuts of the distillation of the dehydration mixture were taken and the infrared spectrum run on each of these cuts. The first fraction in all cases showed a strong absorption at 10.25 μ and in succeeding cuts this signal became less intense and at the same time, absorption at 11.42 μ gradually became more intense. The absorption band at 10.25 μ is the =C-H bending of a trans compound, while that at 11.42 μ is of a cis compound. These various fractions were also subjected to v.p.c. analysis and the first peak decreased in intensity relative to the second peak as successive cuts were analyzed. This showed that the first peak was the trans-isomer. The total percentage was obtained by combining all the fractions of each compound and subjecting these to v.p.c. analysis.

The n.m.r. spectra of these dehydration mixtures were nearly identical; the only difference being the signals of the alkyl side chain at about 0.9 δ. The vinyl proton region consisted of two sets of triplets. Two sets of triplets were observed because of the different environment of the proton in the trans-isomer and in the cis-isomer. In the cis-isomer the vinyl proton is pointed away from the ring, but in the trans-isomer, the proton is pointed into the ring. In each mixture, one triplet is at 5.29 δ (J = 8 cps) and the other at 5.04 δ (J = 8 cps). The triplet at 5.04 δ is assigned to the trans-isomer because of the greater shielding of the vinyl proton by the protons of the ring, thus causing an upfield chemical shift. The area under the trans triplet is greater than the area under the cis triplet, which is in agreement with the v.p.c. analysis showing the trans-isomer to be present in the greatest amount. The allylic protons appear as a multiplet at 3.01 δ.

The dehydration of 1-allylcyclododecanol gave a mixture of five products as shown by v.p.c. analysis. The major products were 24.2% 1-allyl-cis-cyclododecene and 56.7% of 1-allyl-trans-cyclododecene. The infrared spectrum of the various fractions showed that the first cut consisted mainly of the trans-isomer as evidenced by the strong absorption at 10.40 u and decreasing in intensity with each successive fraction. The absorption band at 11.52 μ increased in intensity with each fraction, indicating the increasing presence of the cis-isomer. The infrared spectrum also showed strong absorptions at 6.10 μ, 10.07 μ, and 11.01 μ indicating the presence of $=CH_2$ in the major products. A very weak absorption was observed at 6.27 μ indicating the possibility of conjugation in one or more of the minor products. The n.m.r. spectrum confirms structures XIV and XV as the major products.



(trans)
XIV



(cis)
XV

A complex multiplet appeared at 5.70δ and was assigned to proton b. Two sets of broadened triplets are seen at 5.33δ and 5.09δ. Both have a coupling constant of 8 cps. The signal at 5.33δ is assigned to the cis-isomer (proton H_y) and the signal at 5.09δ is assigned to the trans-isomer (proton H_x). Here again, there are two triplets because of the different chemical environment of the vinyl proton in the cis- and trans-isomers. In the trans-isomer the proton is projected into the ring and is shielded by the ring protons and thus appears up-field from the cis-isomer which does not have the

vinyl proton directed into the ring. A complex multiplet, centered at 4.95δ appears and is assigned to protons, a, in both isomers. Two broadened doublets appear at 2.76δ and at 2.68δ and these were assigned to allylic protons, c, in the cis- and trans-isomers, respectively. These allylic protons are also shielded by the ring in the trans-isomer and thus the signal is shifted up-field. A broadened multiplet appears at 2.06δ and is assigned to the allylic ring protons, e, in both isomers. A few small signals appear in the spectrum, which are not accounted for, and these are probably due to the other three components of the mixture. These three other minor components comprise 6.8%, 2.4%, and 9.9% of the total mixture. It was not possible to identify these compounds and no attempt to speculate on the structure of these compounds is made.

The dehydration of 1-benzylcyclododecanol gave two products as shown by v.p.c. analysis: 23% 1-benzyl-cis-cyclododecene and 77% 1-benzyl-trans-cyclododecene. The infrared spectrum showed an absorption at 10.37 μ, decreasing in intensity with successive fractions, at 11.38 μ, increasing in intensity with each successive fraction. The band at 10.37 μs is accorded to the trans-isomer and that at 11.38 μ is assigned to the cis-isomer. The n.m.r. spectrum confirmed these results. Two sets of broadened triplets appeared at 5.34δ (J = 8 cps) and at 5.14δ (J = 8 cps) and were assigned to the vinyl proton of the cis- and trans-isomers, respectively. Again, there are two sets of triplets because of the different environment of the cis- and trans-isomers. Two broadened singlets appeared at 3.35δ and at 3.24 δ. These were assigned to the benzylic protons of the cis- and trans-isomers, respectively. A broadened multiplet signal was observed at 2.04δ and was assigned to all the allylic protons of the ring.

The results of all dehydrations are shown in Table V. and in Table VI.

Table V.

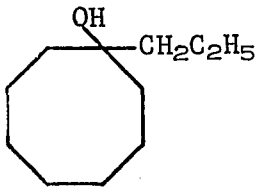
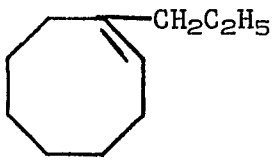
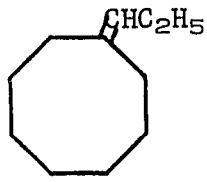
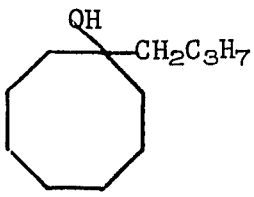
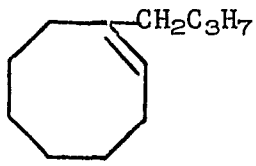
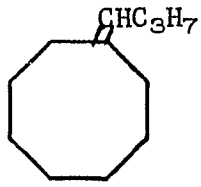
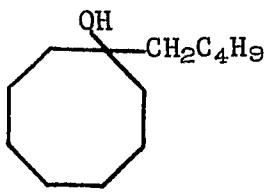
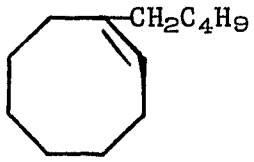
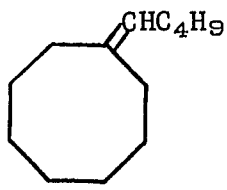
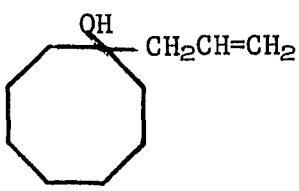
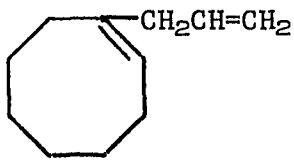
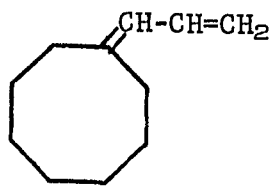
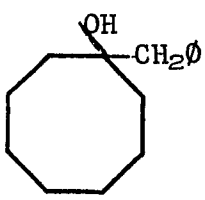
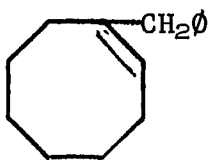
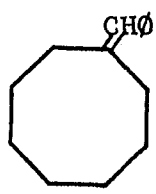
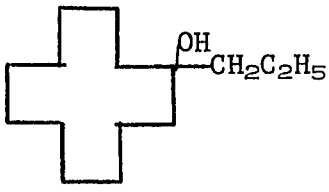
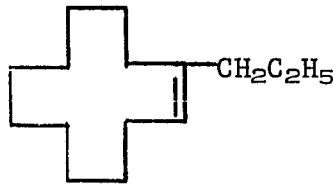
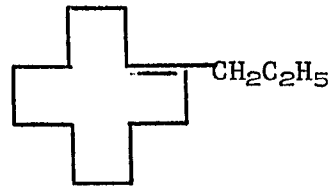
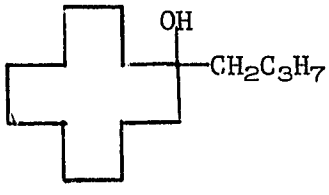
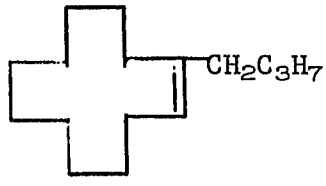
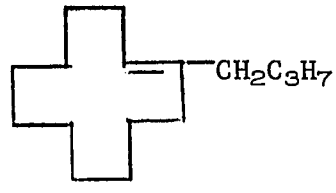
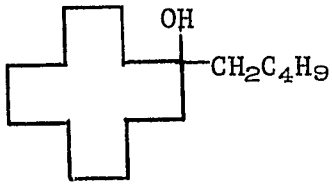
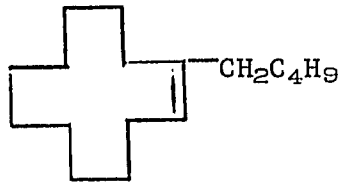
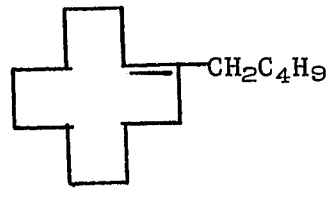
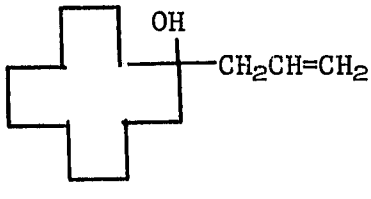
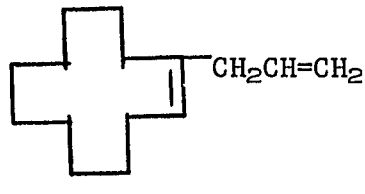
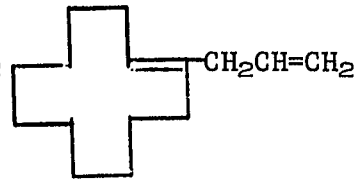
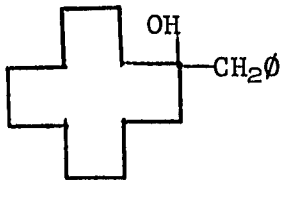
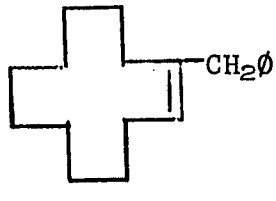
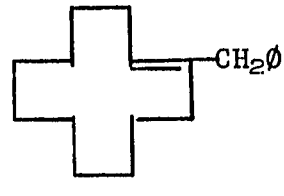
Alcohol	Products (Percentages in parenthesis)	
	 (88%)	 (12%)
	 (91.4%)	 (8.6%)
	 (90.7%)	 (9.3%)
	 (92.5%)	 (7.5%)
	 (100%)	 (0%)

Table VI.

Alcohol	Products	
	 (33%)	 (67%)
	 (29.1%)	 (70.9%)
	 (26.4%)	 (73.6%)
	 (24.2%)	 (56.7%) + others
	 (23%)	 (77%)

In the cyclooctyl series, only the cis-isomer was obtained. This is expected because of the instability of the trans-isomer relative to the cis-isomer in medium rings.[51] About 10% of the exo olefin was formed in each case. This is not surprising because the formation of an sp^2 carbon atom in the cyclooctane ring gives some releif of transannular steric hinderance as can be seen in Table III. Thus this exo olefin is more stable than the alcohol, which contains more transannular hydrogen interactions. More of the endo olefin is formed because of the greater stability of the endo olefin over the exo olefin. Cope and his co-workers[52,53] studied the acid-catalyzed equibibrations of endocyclic and exocyclic olefins. They found an equilibrium constant for 1-methylcyclooctene/methylene-cyclooctane of 598. Thus the endo olefin is considerably more stable than the exo olefin. The only reason that some exocyclic olefin is formed is because of its increased stability over the alcohol. It is surprising that the possibility of conjugation, as in allylidene-cyclooctane and benzylidenecyclooctane, does not affect the amount of endocyclic olefin formed. It was expected that the percentage of endocyclic olefin would decrease and that of exocyclic olefin would increase in these compounds.

In the cyclododecyl series, the trans-isomer was formed to a greater extent than the cis-isomer in all instances studied. Svoboda and Sicher[54] treated samples of pure cis- and trans-cyclododecene with catalytic amounts of concentrated sulfuric acid for 110 hours at room temperature and found a mixture, in both cases, consisting of 40% cis- and 60% trans-cyclododecene. Cope and his workers[55] found the cis/trans olefin ratio of cyclododecene to be 0.534 at 79.9°; 0.517 at 100.4°; and 0.497 at 130°. The eleven- and twelve-membered rings have been found to have a trans-isomer more stable by roughly 1 kcal./mole, similar to simple open chain analogs.[56]

The absence of any exocyclic olefin is probably due to the fact that the change of sp^3 to sp^2 hybridized carbon atom does not

increase the stability nearly as much as in the case of cyclooctane derivatives. This fact can be seen in Table III. The exocyclic cyclododecane is only slightly more stable than the corresponding alcohol. However, the endocyclic cyclododecene would be expected to be much more stable than the exocyclic olefin as in the case of cyclooctene. Thus the more stable products, relative to the reactant, would be expected to be formed in the largest amount, and in this case, it is the 1-substituted-cis- and -trans-cyclododecene.

Thus in the medium rings, some exocyclic olefin is formed, because of the enhanced stability of the exocyclic olefin compared to the tertiary alcohol. However, more endocyclic olefin is formed because of its increased stability over the exocyclic olefin. In the larger rings, the exocyclic olefin is approximately as stable as the tertiary alcohol, but the endocyclic olefin is considerably more stable than the exocyclic olefin. The trans- isomer is more stable in the large rings than the cis-isomer.

EXPERIMENTAL[57]

Cyclooctanone. Part of the material used was obtained from Columbian Carbon; the remainder was prepared from cyclooctene by oxymercuration-demercuration of cyclooctene according to the procedure of Brown and Geoghegan,[35] followed by oxidation of the alcohol by the method of Eisenbraun.[58] To a 2-liter flask fitted with dropping funnel, stirrer, thermometer and condenser was added 159.5 g. (0.5 moles) of mercuric acetate, 300 ml. of water and 300 ml. of tetrahydrofuran. Then 55.0 g. (0.5 moles) of cyclooctene was added slowly, keeping the temperature of the mixture at 25° C. The mixture was stirred for two hours at which time the yellow color disappeared, and then stirred an additional hour. To this mixture, 400 ml. of 3M NaOH was added, followed by the slow addition of 7.6 g. (0.2 moles) of sodium borohydride (dissolved in 400 ml. of 3M NaOH) while keeping the temperature at 25°. This mixture was stirred for 30 minutes after addition of the sodium borohydride solution. The aqueous layer was saturated with sodium chloride and the organic layer separated. The tetrahydrofuran was removed by distillation through a packed column and there remained 58.0 g. of crude cyclooctanol.

To a 2-liter flask fitted with dropping funnel, stirrer, and thermometer was added a solution of the 58.0 g. of crude cyclooctanol in 1.25 liters of acetone and cooled to 20°. Chromic acid oxidizing reagent (from 67 g. chromium trioxide, 125 ml. distilled water and 58 ml. of concentrated sulfuric acid) was added, at a slow rate so that the temperature does not rise above 35°. The addition was continued until the characteristic orange color persisted for about 20 minutes. The mixture was decanted and the residual green salts rinsed with two 70 ml. portions of acetone. The rinsings were added to the main acetone solution. Isopropyl alcohol was added dropwise to the acetone solution until the excess chromic acid was destroyed.

Then in small portions, 63 g. of sodium bicarbonate was added with stirring until the solution was neutral. The solution was filtered and washed with 25 ml. of acetone. The filtrate was concentrated by distillation through a 65 cm. packed column until the pot temperature rose to 80°. The cooled residue was then extracted with three 100 ml. portions of ether. The ether extracts were combined and washed with two 10 ml. portions of water and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the residue vacuum distilled to give 50.3 g. (81%, based on cyclooctene) of cyclooctanone; b.p. 78-79°/(10 mm); (lit. b.p. 115-118°/(64 mm);[59] 118-120°/(64 mm);[48] 76-77°/(10 mm).[58]

1-Propylcyclooctanol.— To a propylmagnesium bromide solution (from 49.2 g. (0.40 moles) of propyl bromide, 9.71 g. (0.42 g.-atm.) of magnesium and 200 ml. of ether) was added slowly with stirring, 31.5 g. (0.25 moles) of cyclooctanone dissolved in 100 ml. of ether. After the addition was complete, the mixture, with continous stirring, was refluxed for five hours. The mixture was cooled and then poured over 200 g. of crushed ice and 50 ml. of a saturated solution of ammonium chloride. The layers were separated and the aqueous layer was extracted with 100 ml. of ether. The combined ether extracts were washed with 25 ml. of 10% sodium carbonate solution and then with 10 ml. of water. After drying the etheral solution over potassium carbonate, the ether was removed on a rotorary evaporator, leaving 38.1 g. of residue. The infrared spectrum of the residue showed the presence of a hydroxyl group and a carbonyl group indicating that this was a mixture of 1-propylcyclooctanol and cyclooctanone. Therefore a second batch of Grignard reagent was added to this mixture. The above procedure was followed using 49.2 g. (0.40 moles) of propyl bromide, 9.71 g. (0.42 g.-atm.) of magnesium and 38.1 g. of the mixture. From this reaction, there was obtained 34.3 g. of a liquid which still contained the presence of a carbonyl group as shown by

the infrared spectrum, although the amount of ketonic material had decreased. The Grignard reaction was run again with the same quantities as above, except 34.3 g. of mixture was used. There was obtained from this reaction 29.6 g. of a liquid that contained about 1% cyclooctanone as impurity according to the infrared spectrum. A 5.0 g. sample of the mixture was distilled to 1.5 g. of pure 1-propylcyclooctanol, a colorless liquid; b.p. 69°/(0.5 mm); n_D^{20} 1.4816; λ_{max} 2.95, 3.43, 3.49, 6.78, 6.88, 8.80, 9.88, 10.25, and 11.85 μ. The distillation was accompanied by extensive dehydration. The overall yield before distillation was 69.7%.

1-(1-propylcyclooctyl) phenyl urethan. —— 1-Propylcyclooctanol, 2.0 g. (0.012 moles) and phenyl isocyanate, 2.9 g. (0.024 moles) were mixed and allowed to stand at room temperature in a tightly stoppered flask for one week, after which time a solid was deposited. The cooled solution was filtered, the precipitate dissolved in hot pentane and this solution filtered to remove any insoluble material. Upon cooling the pentane solution there was obtained 2.4 g. (69%) of a white, plate-like, crystalline product; m.p. 65.0-65.5°.

Anal. Calcd for $C_{18}H_{27}NO_2$: C,74.70; H,9.40. Found: C,74.65; H,9.48.

Dehydration of 1-propylcyclooctanol. —— To 4.8 g. (0.028 moles) of 1-propylcyclooctanol was added 1 ml. of 85% phosphoric acid. This mixture was heated in an oil bath at 120° for 30 minutes. The resulting mixture was cooled and extracted with 30 ml. of pentane. The pentane extract was washed with successive portions of 2 ml. of water, 2 ml. of 10% sodium carbonate solution and again with 2 ml. of water. The pentane solution was dried over anhydrous sodium carbonate, the pentane removed on a rotary evaporator and the residue vacuum distilled to give 2.9 g. (68%) of a clear liquid, which had

had the following physical properties: b.p. 67-68°/(5.0 mm); n_D^{20} 1.4746; λ_{max} 3.42, 3.50, 6.00, 6.02 (shoulder), 6.81, 6.90, 7.26, 7.36, 9.03, 9.15, 11.09, 11.20, and 12.08 μ. From vapor phase chromatography, infrared spectrum, and nuclear magnetic resonance spectrum, the compound was identified as a mixture of 88% 1-propyl-cis-cyclooctene and 12% propylidenecyclooctane.

1-Butylcyclooctanol.— All Grignard reactions were run by using the procedure described in the preparation of 1-propylcyclooctanol. To butylmagnesium bromide (from 9.71 g. (0.42 g.-atm.) of magnesium and 54.8 g. (0.40 moles) of butyl bromide) was added 31.5 g. (0.25 moles) of cyclooctanone. From this reaction, 35.6 g. of a mixture of 1-butylcyclooctanol and cyclooctanone was obtained. This was reacted twice with the Grignard reagent (same quantities as above) to give 26.6 g. (58%) of 1-butylcyclooctanol containing about 1% cyclooctanone. A five gram sample was distilled to give 1.2 g. of pure 1-butyloctanol; b.p. 77-78°/(0.3 mm); n_D^{20} 1.4820; λ_{max} 2.94, 3.42, 3.50, 6.79, 6.89, 7.25, 8.11, 8.80, 9.54, 9.90, 10.15, 11.25, and 11.83 μ. The distillation was accompanied by extensive dehydration.

1-(1-Butylcyclooctyl) phenyl urethan.— All phenyl urethans were prepared in the manner as described in the preparation of 1-(1-propylcyclooctyl) phenyl urethan. From 2.0 g. (0.11 moles) of 1-butylcyclooctanol and 2.6 g. (0.022 moles) of phenyl isocyanate there was obtained 2.4 g. (73%) of a white, plate-like, crystalline product; m.p. 74.5-75.0°.

Anal. Calcd for $C_{19}H_{29}NO_2$: C,75.20; H,9.63. Found: C,75.10; H,9.57.

Dehydration of 1-butylcyclooctanol.— All dehydrations were performed in the same manner as described in the dehydration of 1-pr(67%) of a clear liquid; b.p. 94-95°/(8.0 mm); n_D^{20} 1.4742; octar λ_{max} 3.42, 3.50, 5.99, 6.01 (shoulder), 6.81, 6.90, 7.25, 7.36, (67% 9.03, 10.73, 11.11, 11.19, and 11.92 μ. By use of the infrared λ_{max} 3.42, 3.50, 5.99, 6.01 (shoulder), 6.81, 6.90, 7.25, 7.36, 9.03, 10.73, 11.11, 11.19, and 11.92 μ. By use of the infrared spectrum, n.m.r. and v.p.c analysis, the compound was identified as mixture of 91.4% 1-butyl-cis-cyclooctene and 8.6% butylidene-cyclooctane.

1-Amylcyclooctanol.— From amylmagnesium bromide (17.5 g. (0.72 g.-atm.) of magnesium and 105.5 g. (0.70 moles) of amyl bromide) and 50.5 g. (0.40 moles) of cyclooctanone there was obtained 55.6 g. of a mixture of 1-amylcyclooctanol and cyclooctanone. This mixture was reacted twice with amylmagnesium bromide, prepared in the same proportions as above to give 44.3 g. (79%) of 1-amylcyclooctanol, containing less than 1% cyclooctanone as impurity. A 5.0 g. sample was vacuum distilled to give 1.9 g. of pure 1-amylcyclooctanol; b.p. 90.0-90.5°/(0.4 mm); n_D^{20} 1.4768; λ_{max} 2.93, 3.42, 3.50, 6.80, 6.89, 7.25, 8.11, 8.80, 9.56, 9.85, and 10.55 μ. The distillation was accompanied by extensive dehydration.

1-(1-Amylcyclooctyl) phenyl urethan.— 2.0 g. (0.010 moles) of 1-amylcyclooctanol and 2.4 g. (0.020 moles) of phenyl isocyanate were reacted to give 1.4 g. (44%) of a white crystalline product; m.p. 104-105°.

Anal. Calcd for $C_{20}H_{31}NO_2$: C,75.67; H,9.84. Found: C,75.41; H,9.67.

Dehydration of 1-amylcyclooctanol.— From 5.0 g. (0.025 moles) of 1-amylcycloctanol and 1 ml. of 85% phosphoric acid, there was obtained 3.4 g. (76%) of a clear liquid; b.p. 108-109°/(9.0 mm); n_D^{20} 1.4723; λ_{max} 3.42, 3.50, 5.99, 6.01 (shoulder), 6.81, 6.89, 7.25, 7.36, 9.01, 11.11, 11.19, and 12.02 μ. From the infrared spectrum, n.m.r. spectrum and v.p.c. analysis the compound was determined to be a mixture of 90.7% 1-amyl-cis-cyclooctene and 9.3% amylidenecyclooctane.

1-Allylcyclooctanol.— Allylmagnesium bromide (from 9.71 g. (0.42 g.-atm.) of magnesium and 48.4 g. (0.40 moles) of allyl bromide) and 31.5 g. (0.25 moles) of cyclooctanone were reacted to give 35.8 g. of a mixture of 1-allylcyclooctanol and cyclooctanone. This mixture was reacted with allylmagnesium bromide, using the same quantities as above, to give 31.6 g. (75%) of 1-allylcyclooctanol which contained about 1% cyclooctanone as impurity. A 5.0 g. sample was distilled to give 1.1 g. of pure 1-allylcyclooctanol; b.p. 71-72°/(.6 mm); n_D^{20} 1.4936; λ_{max} 2.94, 3.26, 3.43, 3.50, 5.46, 6.09, 6.79, 6.90, 8.12, 8.72, 9.50, 9.85, 10.00, 10.15, 11.00, 11.25, 11.84, 12.38, and 13.15 μ. This distillation was accompanied by extensive dehydration.

1-(1-Allylcycloocty) phenyl urethan.— From 2.0 g. (0.012 moles) of 1-allylcyclooctanol and 2.8 g. (0.024 moles) of phenyl isocyanate, there was obtained 1.4 g. (41%) of white, plate-like, crystals; m.p. 80-81°.

Anal. Calcd for $C_{18}H_{25}NO_2$: C,75.22; H,8.77. Found: C,75.03; H,8.79.

Dehydration of 1-allylcycloctanol.— 1-Allylcyclooctanol, 5.0 g. (0.030 moles), and 85% phosphoric acid, 1 ml., were reacted to give 3.6 g. (80%) of a clear liquid; b.p. 79-80°/(10 mm); n_D^{20} 1.4891; λ_{max} 3.25, 3.42, 3.50, 5.99, 6.08, 6.80, 6.89, 6.98, 7.07, 7.25, 7.36, 7.81, 8.14, 8.67, 8.72, 9.78, 10.06, 10.38, 11.00, 11.78, 11.98, 12.21, 12.77, and 13.25 μ. From infrared spectrum, n.m.r. spectrum and v.p.c. analysis, the compound was determined to be a mixture of 92.5% 1-allylcyclooctene and 7.5% allylidene-cyclooctane.

1-Benzylcyclooctanol.— Benzylmagnesium chloride (from 9.71 g. (0.42 g.-atm.) of magnesium and 50.8 g. (0.40 moles) of benzyl chloride) and 31.5 g. (0.25 moles) of cyclooctanone were reacted to give 41.6 g. (76%) of a slightly yellow liquid, shown by infrared spectrum to contain less than 1% cyclooctanone as impurity. A 5.0 g. sample was vacuum distilled to give 1.8 g. of pure 1-benzylcyclooctanol; b.p. 113-114°/(0.1 mm); m.p. 27-28°; λ_{max} 2.90, 3.30, 3.43, 3.50, 6.23, 6.69, 6.79, 6.89, 8.83, 9.26, 9.46, 9.70, 9.86, 10.08, 11.26, 13.00, 13.58, and 14.19-14.32 μ.

1-(1-Benzylcyclooctyl) phenyl urethan.— 1-Benzylcyclooctanol, 2.0 g. (0.009 moles), and phenyl isocyanate, 2.1 g. (0.018 moles), were reacted to give 1.9 g. (63%) of a white, plate-like, crystalline product; m.p. 130.5-131.0°.

Anal. Calcd for $C_{22}H_{27}NO_2$: C,78.34; H,8.07. Found: C,78.52; H,8.14.

Dehydration of 1-benzylcyclooctanol.— From 5.0 g. (0.023 moles) of 1-benzylcyclooctanol and 1 ml. of 85% phosphoric acid, there was obtained 3.1 g. (68%) of a clear liquid; b.p. 104-105°/(1.5 mm);

n_D^{20} 1.5423; λ_{max} 3.30, 3.43, 3.50, 6.00 (weak), 6.22, 6.64, 6.81, 6.87, 9.31, 9.71, 11.16, 13.12,13.56, 13.92, and 14.34 μ. From the infrared spectrum, n.m.r. spectrum and v.p.c. analysis the compound was determined to be a single compound, 1-benzylcyclooctene.

Attempted preparation of benzylidenecyclooctane:

Method A.— Via the Wittig Reaction.

Triphenylbenzylphosphonium chloride.— 40.0 g. (0.153 moles) of triphenylphosphine, 40.0 g. (o.316 moles) of benzyl chloride and 75 ml. of sodium dried benzene were allowed to stand at room temperature for 6 hours. The solution was cooled and the resulting precipitate was collected and washed with cold benzene. Recrystallization from chloroform gave 58.0 g. (97.0%) of the salt; m.p. 316-318; (lit.[60] m.p. 317-318).

Wittig Reaction of Triphenylbenzylphosphonium Chloride with Cyclooctanone.— In a three-neck flask fitted with condenser, stirrer, and dropping funnel, was added 24 g. of the phosphonium salt and 50 ml. of sodium-dried ether. The flask was continously swept with dry nitrogen. Then 25 ml. of a 15% (by weight) solution of n-butyllithium in hexane was dropped in slowly. This mixture was stirred for two hours at room temperature. To the deep red mixture, 6.9 g. (0.055 moles) of cyclooctanone, dissolved in 15 ml. of ether, was added slowly. This mixture was stirred and refluxed for 18 hours, cooled, and then filtered. The precipitate was washed with 100 ml. of ether. The combined ether extracts were washed with 100 ml. portions of water until the water wash was neutral. The ethereal solution was dried over calcium chloride; the ether removed and the residue subjected to vacuum distillation to give

4.6 g. of cyclooctanone and 1.3 g. of a black viscious residue.

This reaction was also run in benzene as solvent in place of ether, but again only cyclooctanone was obtained.

Method B

Sodium salt of benzylsulfonic acid.[61] — Into 350 ml. of water was stirred 104 g. (0.825 moles) of sodium sulfite followed by slow addition of benzyl chloride. The solution was then stirred for 6 hours at 95°. Upon cooling the mixture, white, plate-like, crystals were formed. A second crop of crystals was also obtained by evaporating the filtrate to 1/3 its original volume. The total yield of crystals was 146.2 g. (91%).

Benzylsulfonyl chloride.[62] — To 30 g. (0.15 moles) of the thoroughly dried sodium salt of benzylsulfonic acid was added, with stirring and in small portions, 40 g. (0.19 moles) of phosphorous pentachloride. The slurry was heated with constant stirring for 45 minutes at 50°. The slurry was then poured carefully onto crushed ice and the resulting mixture was extracted with two-100 ml. portions of ether. The combined ether extracts were washed with 15 ml. of water and then dried over anhydrous magnesium sulfate. The ether was evaporated on a rotary evaporator leaving 20.9 g. of a white crystalline residue. This was not recrystallized until ready to use. Ten grams of crude benzylsulfonyl chloride was dissolved in 350 ml. of petroleum ether and allowed to crystallize to give 9.6 g. of long needle-like, snow-white crystals; m.p. 91-92°; (lit.[62] 91°).

Cyclooctanone hydrazone. — Ten g. (0.065 moles) of powered barium oxide, 14.0 g. (0.28 moles) of freshly distilled hydrazine

hydrate, and 20 ml. of absolute ethanol were placed in a 3-neck flask equipped with dropping funnel, stirrer, and condenser. Then 31.5 g. (0.25 moles) of cyclooctanone, dissolved in 10 ml. of ethanol was added slowly and the resulting mixture stirred at reflux temperature for 8 hours. The mixture was cooled and diluted with 100 ml. of ether. The solution was then filtered, ether removed on a rotary evaporator, and vacuum distilled to give 22.5 g. (64.5%) of cyclooctanone hydrazone; b.p. 95-96°/(2.5 mm); n_D^{20} 1.5196; λ_{max} 2.96, 3.12, 3.44, 3.50, 6.10, 6.20, 6.81, 6.91, 7.00, 7.38, 8.20, 8.64, 8.98, 9.34, 9.57, and 9.80 μ.

Diazocyclooctane and subsequent reaction with benzylsulfene.— In a 3-neck flask equipped with stirrer, dropping funnel, thermometer, condenser and nitrogen inlet, 39.4 g. (0.17 moles) of dried silver oxide (81 g. silver nitrate in 200 ml. of water added to 22.5 g. of sodium hydroxide in 1500 ml. of water) was suspended in 200 ml. of dry ether, along with 20 g. of anhydrous magnesium sulfate. The entire reaction was run under a nitrogen atmosphere. Then 20 g. (0.143 moles) of cyclooctanone hydrazone was added slowly at -15°. The stirred solution was kept at -15 to -10° for 1 1/2 hours at which time an orange color was noted. After addition of 25 ml. of dry triethylamine, 9.6 g. (0.050 moles) of benzylsulfonyl chloride, in 50 ml. of ether, was added slowly and the mixture was allowed to warm to -5°, at which time the solution became blood-red indicating the presence of the diazo compound. Upon addition of each small portion of benzylsulfonyl chloride, nitrogen was noted as being evolved. After addition was complete, the mixture was stirred 30 minutes at -5°, and then stirred an additional hour while the mixture warmed to room temperature. The mixture was filtered, the ether removed on a rotary evaporator and the residue was vacuum distilled. The infrared spectrum and n.m.r. spectrum of the distillate, collected in the dry ice trap, showed the only compound present was cyclooctene.

Cyclododecanone.— Part of the material was purchased from the Aldrich Chemical Co.; the remainder was prepared from cyclododecene by oxymercuration-demercuration of cyclododecene according to the procedure of Brown and Geoghegan[35] followed by oxidation of the alcohol by the method of Eisenbraun.[58] The procedure followed is the same as that for cyclooctanone, which was previously described. The following amounts of material were used: 159.5 g. (0.50 moles) of mercuric acetate, 83.0 g. (0.50 moles) of cyclododecene and 7.6 g. of sodium borohydride. After oxidation with chromic acid, 68.2 g. (75%) of cyclododecanone was obtained; m.p. 61-62° (lit.[63] m.p. 61°, b.p. 125°/(12 mm)).

1-Propylcyclododecanol.— A solution of propylmagnesium bromide (from 12.15 g. (0.50 g.-atm.) of magnesium and 59.0 g. (0.48 moles) of propyl bromide) was reacted with 69.2 g. (0.38 moles) of cyclododecanone to give 70.2 g. of a white solid, which upon recrystallization from acetone yielded 53.9 g. (63%) of pure 1-propylcyclododecanol; m.p. 67-68°; $\lambda_{max}^{CCl_4}$ 2.76, 3.42, 3.50, 6.80, 6.90, 7.41, 8.59, and 10.09 μ.

1-(1-Propylcyclododecyl) phenyl urethan.— The reaction of 2.0 g. (0.009 moles) of 1-propylcyclododecanol and 2.1 g. (0.018 moles) of phenyl isocyanate gave 1.4 g. (43%) of a white, powdered, crystalline material; m.p. 132-133°.

Anal. Calcd for $C_{22}H_{35}NO_2$: C,76.47; H,10.21. Found: C,76.36; H,10.31.

Dehydration of 1-propylcyclododecanol. A mixture of 5.0 g. (0.022 moles) and 1 ml. of 85 % phosphoric acid were heated at 110° for 45 minutes. There was obtained from this reaction 2.9 g. (63%); b.p. 103-104°/(3 mm); n_D^{20} 1.4870; λ_{max} 3.42, 3.50, 6.02, 6.83, 6.93, 7.26, 7.44, 10.25, 11.42, 12.69-12.73, 13.00-13.10, 13.75, and 14.36 μ.

From the infrared spectrum, n.m.r. spectrum and v.p.c. analysis the compound was determined to be a mixture of 33% 1-propyl-cis-cyclododecene and 67% 1-propyl-trans-cyclododecene.

1-Butylcyclododecanol.— Butylmagnesium bromide (from 8.5 g. (0.35 g.-atm.) of magnesium and 45.2 g. of butyl bromide (0.33 moles)) and 36.4 g. (0.20 moles) of cyclododecanone were reacted to give 37.1 g. of a white solid. After recrystallization from acetone 32.1 g. (67%) of white, prisim-like, crystals of 1-butylcyclododecanol was obtained; m.p. 72-73°; $\lambda_{max}^{CCl_4}$ 2.76, 3.42, 3.49, 6.79, 6.90, 7.42, 8.61, 9.50, 10.04, and 11.11 μ.

1-(1-Butylcyclododecyl) phenyl urethan.— From the reaction of 2.0 g. (0.008 moles) of 1-butylcyclododecanol and 1.9 g. (0.016 moles) of phenyl urethan, there was obtained 1.1 g. (38%) of a white crystalline product; m.p. 126-127°.

Anal. Calcd for $C_{23}H_{37}NO_2$: C,76.83; H,10.37. Found: C,76.60; H,10.37.

Dehydration of 1-butylcyclododecanol.— Five g. (0.021 moles) of 1-butylcyclododecanol was dehydrated with 1 ml. 85% phosphoric acid to give 3.0 g. (67%) of a clear liquid; b.p. 97-98°/(0.3 mm); n_D^{20} 1.4872; λ_{max} 3.42, 6.02, 6.81, 6.90, 7.25, 7.42, 10.25, 11.42, 13.76, and 14.32 μ. The infrared spectrum, n.m.r. spectrum and v.p.c. analysis showed the compound to be a mixture of 29.1% 1-butyl-cis-cyclododecene and 70.9% 1-butyl-trans-cyclododecene.

1-Amylcyclododecanol.— The reaction of amylmagnesium bromide (from 8.5 g. (0.35 g.-atm.) of magnesium and 49.8 g. (0.33 moles)

of amyl bromide) and 36.4 g. (0.20 moles) of cyclododecanone gave 45.6 g. of a white solid. Recrystallization from acetone gave 28.4 g. (56%) of white, prisim-like, crystals of 1-amylcyclododecanol; m.p. 74-75°; $\lambda_{max}^{CCl_4}$ 2.76, 3.43, 3.50, 6.79, 6.91, 7.42, 8.61, 9.50, 10.00, 10.65, and 11.06 μ.

1-(1-Amylcyclododecyl) phenyl urethan.— The reaction of 2.0 g. (0.008 moles) of 1- amylcyclododecanol and 1.9 g. (0.016 moles) of phenyl isocyanate yielded 1.5 g. (50%) of a white, powdered, solid; m.p. 142.5-143.0°.

Anal. Calcd for $C_{24}H_{39}NO_2$: C,77.16; H,10.52. Found: C,76.96; H,10.46.

Dehydration of 1-amylcyclododecanol.— From 5.0 g. (0.020 moles) of 1-amylcyclododecanol and 1 ml. of 85% phosphoric acid there was obtained 3.7 g. (79%) of a clear liquid; b.p. 103-104°/(0.3 mm); n_D^{20} 1.4867; λ_{max} 3.42, 3.50, 6.02, 6.90, 7.25, 7.42, 10.25, 11.41, 13.78, and 14.38 μ. The infrared spectrum, n.m.r. spectrum, and v.p.c. analysis showed the compound to be a mixture of 26.4% 1-amyl-cis-cyclododecene and 73.6% 1-amyl-trans-cyclododecene.

1-Allylcyclododecanol.— A solution of allylmagnesium bromide (from 9.6 g. (0.40 g.-atm.) of magnesium and 46.0 g. (0.38 moles) of allyl bromide) and 51.0 g. (0.28 moles) of cyclododecanone were reacted to give 57.2 g. of a white solid. This solid was recrystallized from acetone to give 43.2 g. (69%) of a white, prisim-like, solid, 1-allylcyclododecanol; m.p. 65-66°; $\lambda_{max}^{CCl_4}$ 2.77, 3.42, 3.50, 6.08, 6.79, 6.90, 7.41, 8.61, 9.05, 9.46, 10.03, 10.83, 10.92, and 11.18 μ.

1-(1-Allylcyclododecyl) phenyl urethan.— Two g. (0.010 moles) of 1-allylcyclododecanol and 2.4 g. (0.020 moles) of phenyl isocyanate were reacted to give 2.6 g. (77%) of white, powdered, product; m.p. 124-125°.

Anal. Calcd for $C_{22}H_{33}NO_2$: C,76.92; H,9.68. Found: C,76.58; H,9.62.

Dehydration of 1-allylcyclododecanol.— Five g. (0.026 moles) of 1-allylcyclododecanol and 1 ml. of 85% phosphoric acid were reacted to give 2.9 g. (64%) of a clear liquid; b.p. 105-106°/(2.0 mm); n_D^{20} 1.5051; λ_{max} 3.42, 3.50, 6.10, 6.81, 6.91, 7.44, 10.08, 10.39, 11.03, 11.52, 13.77, and 14.35 μ. The infrared spectrum, n.m.r. spectrum, and v.p.c. analysis showed the compound to be a mixture of 24.2% 1-allyl-cis-cyclododecene, 56.7% of 1-allyl-trans-cyclododecene, and three unidentified compounds of the following percentages: 6.8%, 2.4%, and 9.9%.

1-Benzylcyclododecanol.— An ethereal solution of benzylmagnesium chloride (from 9.6 g. (0.40 g.-atm.) of magnesium and 49.5g. (0.39 moles) of benzyl chloride) was reacted with 51.0 g. (0.28 moles) of cyclododecanone to give 72.9 g. of a white solid. This solid upon recrystallization from acetone yielded 59.7 g. (77%) of white prism-like crystals of 1-benzylcyclododecanol; m.p. 79-80°; $\lambda_{max}^{CCl_4}$ 2.77, 3.30, 3.42, 3.50, 6.22, 6.68, 6.80, 6.88 (shoulder), 6.90, 7.41, 7.82, 9.26, and 11.17 μ.

1-(1-Benzylcyclododecyl) phenyl urethan.—Two g. (0.007 moles) of 1-benzylcyclododecanol and 1.7 g. (0.014 moles) of phenyl iso-

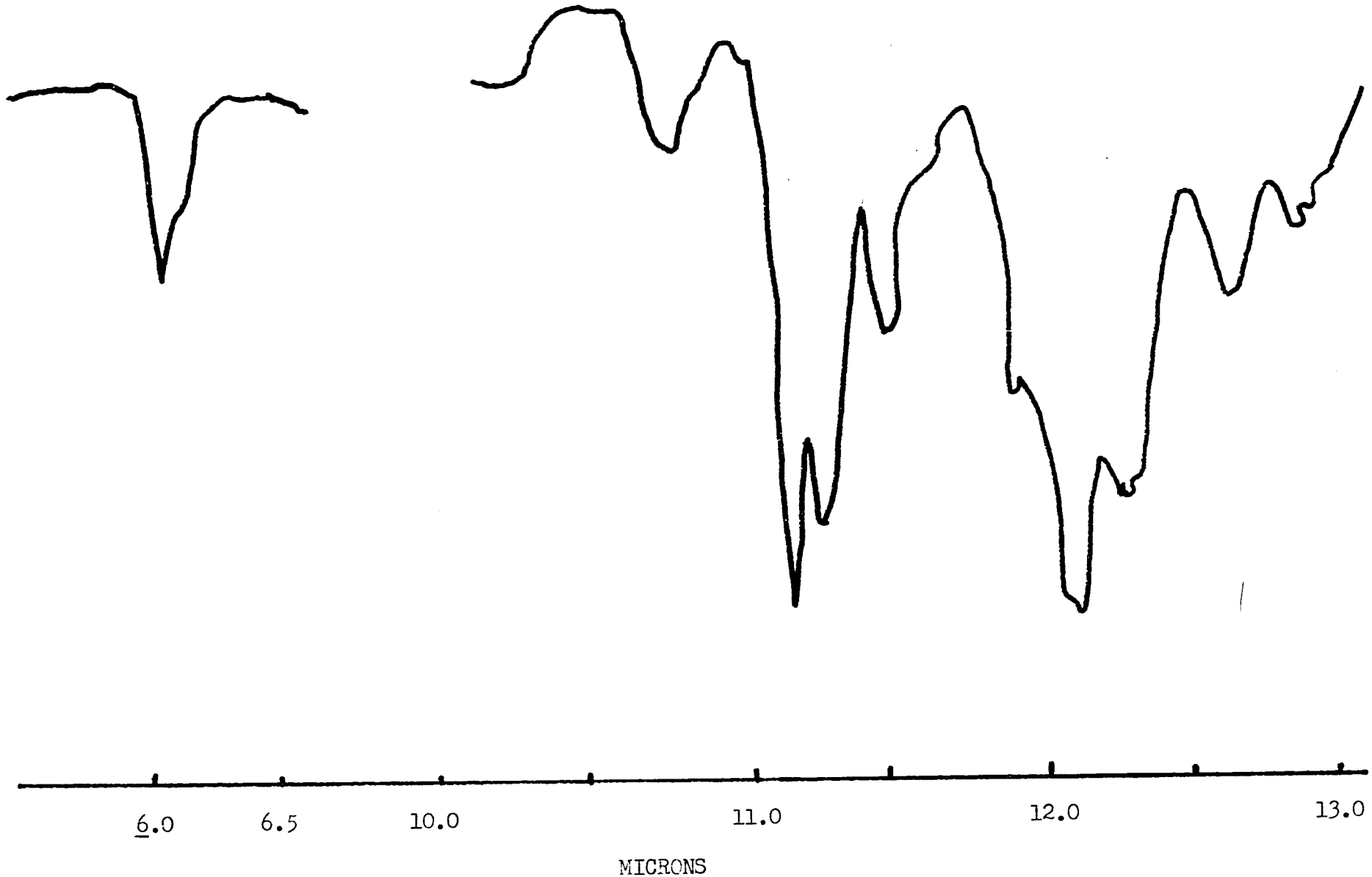
cyanate were reacted to give 1.5 g. (58%) of white, powdered, crystals of the urethan; m.p. 175-176°.

Anal. Calcd for $C_{26}H_{35}NO_2$: C,79.34; H,8.96. Found: C,79.20; H,8.91.

Dehydration of 1-benzylcyclododecanol.—A 5.0 g. sample (0.018 moles) of 1-benzylcyclododecanol was reacted with 1 ml. of 85% phosphoric acid to give 3.8 g. (81%) of a colorless, viscous liquid; b.p. 131-132°/(0.2 mm); n_D^{20} 1.5385; λ_{max} 3.30, 3.42, 3.50, 6.04, 6.24, 6.65, 6.82, 6.90, 7.44, 8.04, 9.22, 9.71, 10.37, 11.38, 12.21, 13.14-13.19, 13.85, and 14.34 μ. The infrared spectrum, n.m.r. spectrum and v.p.c. analysis showed the compound to be a mixture of 23% 1-benzyl-cis-cyclododecene and 77% 1-benzyl-trans-cyclododecene.

SPECTRA

INFRARED SPECTRUM OF ALKYLCYCLOOCTENE



INFRARED SPECTRUM OF ALLYLCYCLOOCTENE

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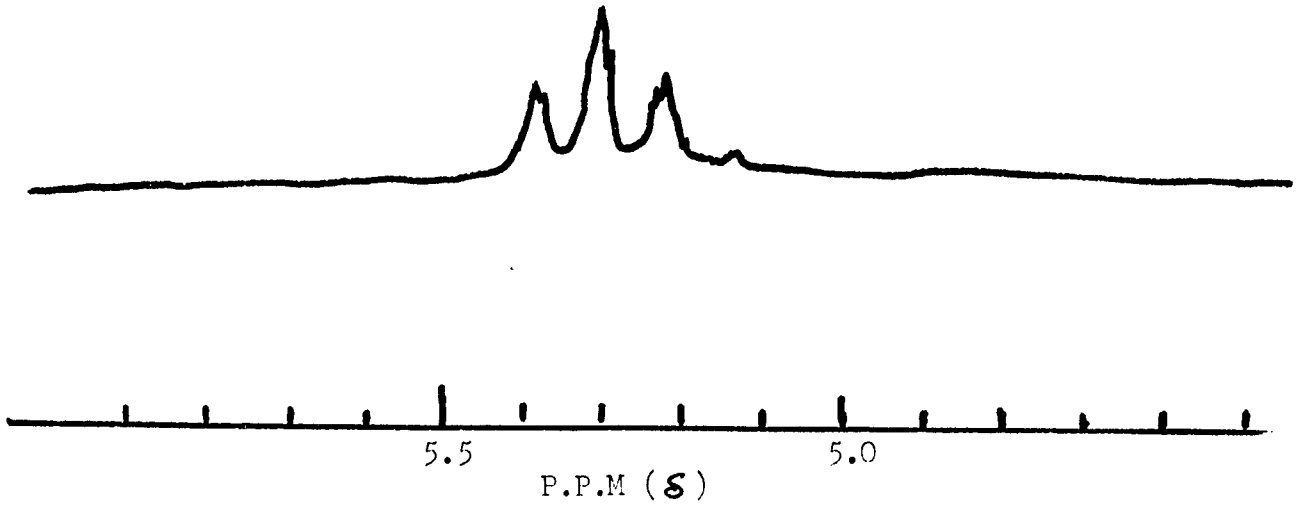

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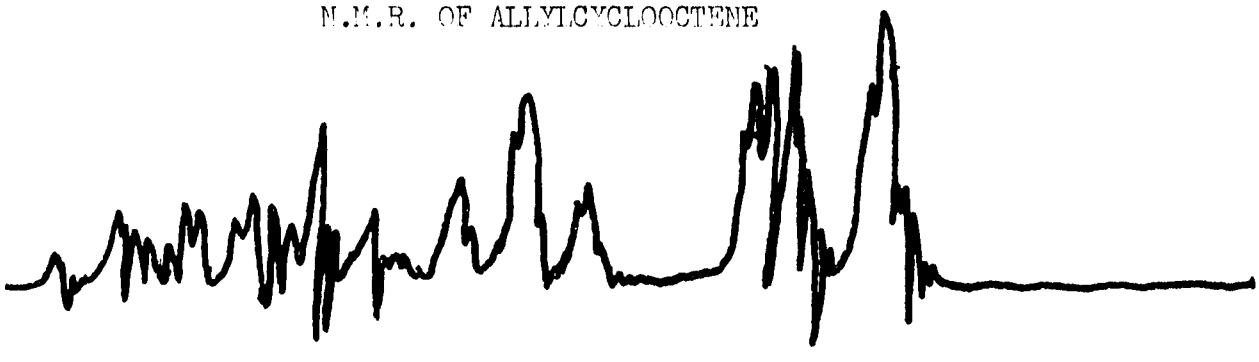

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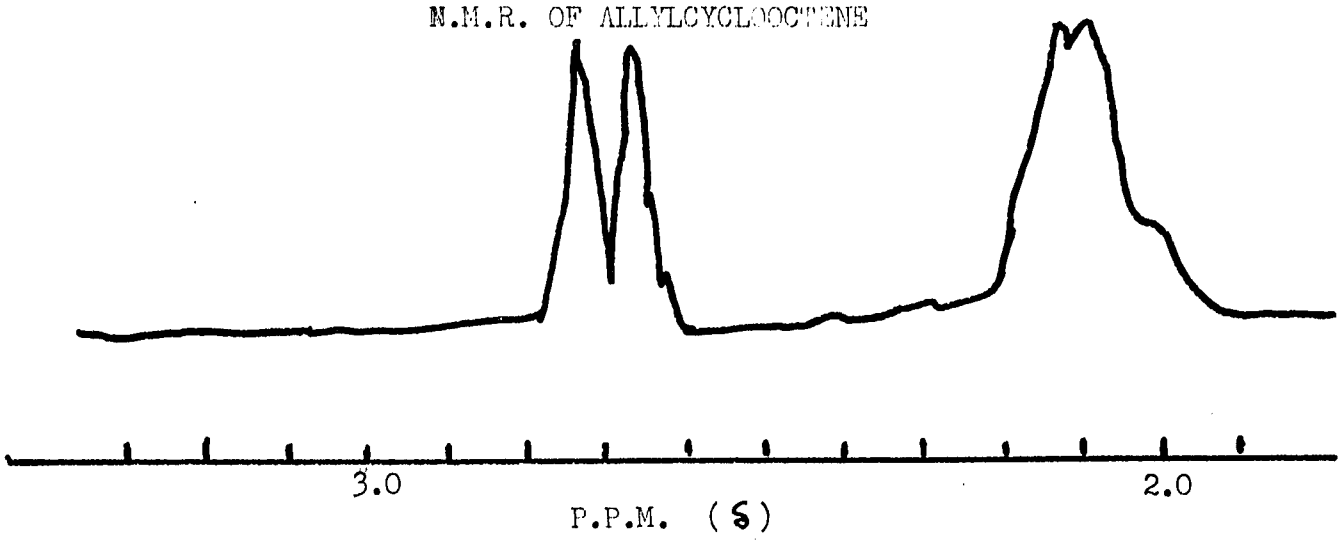

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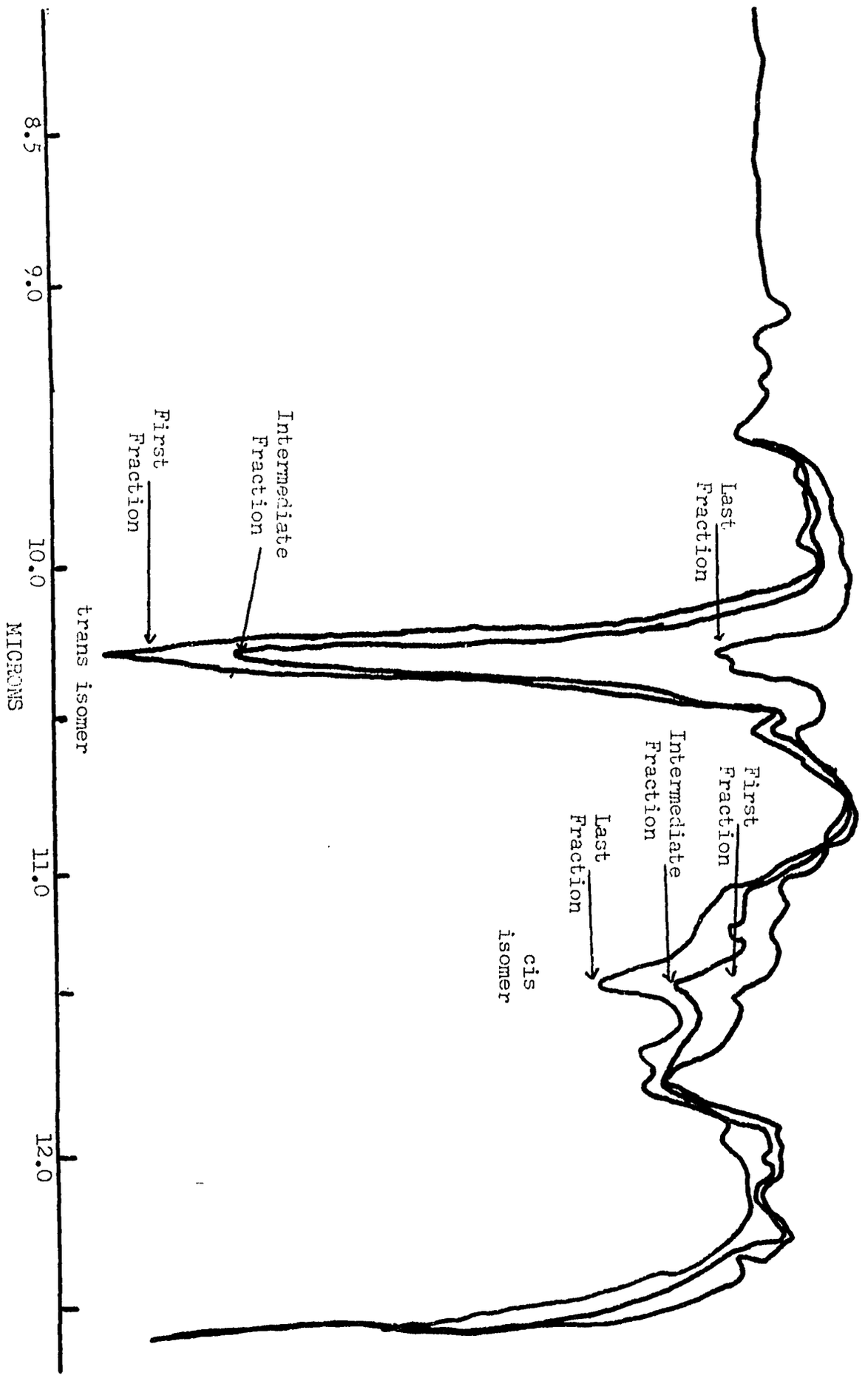

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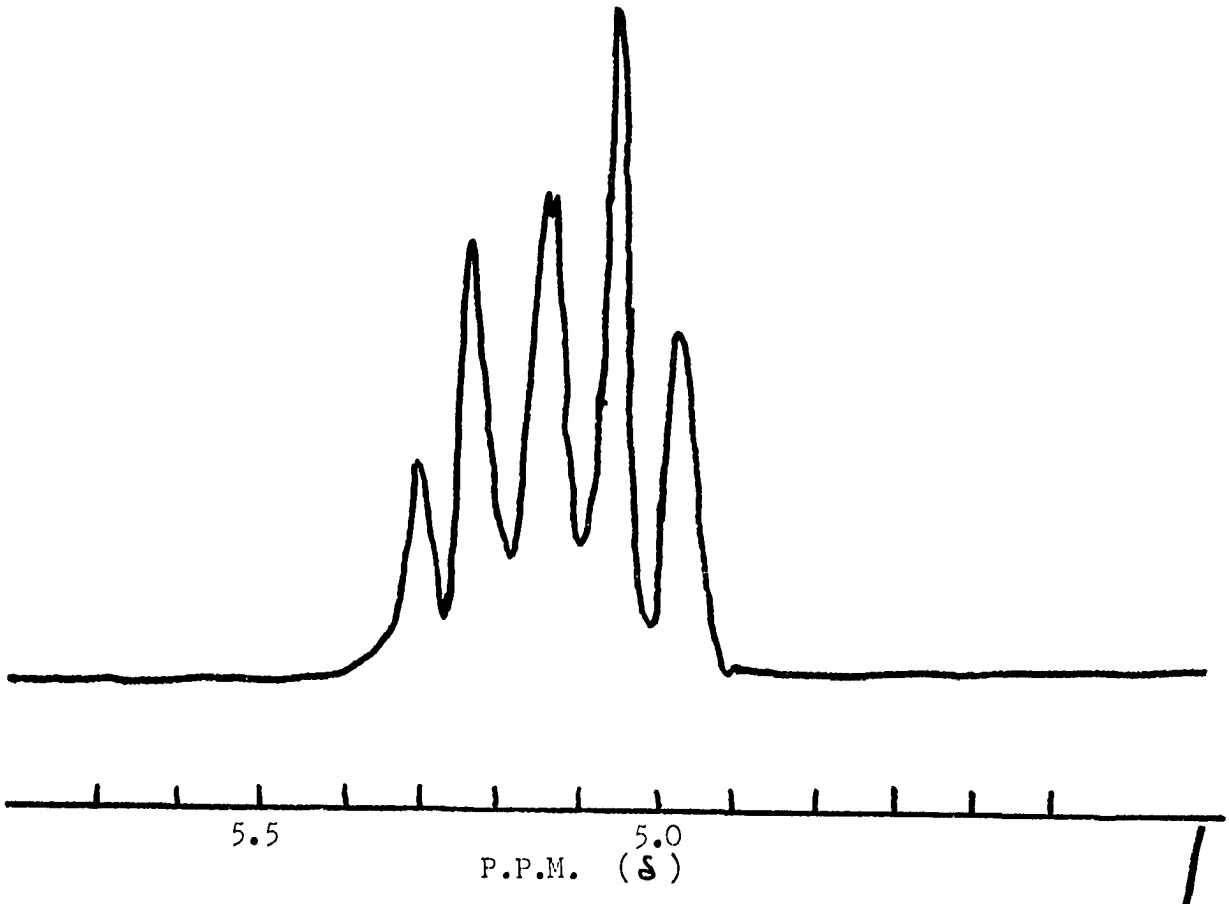

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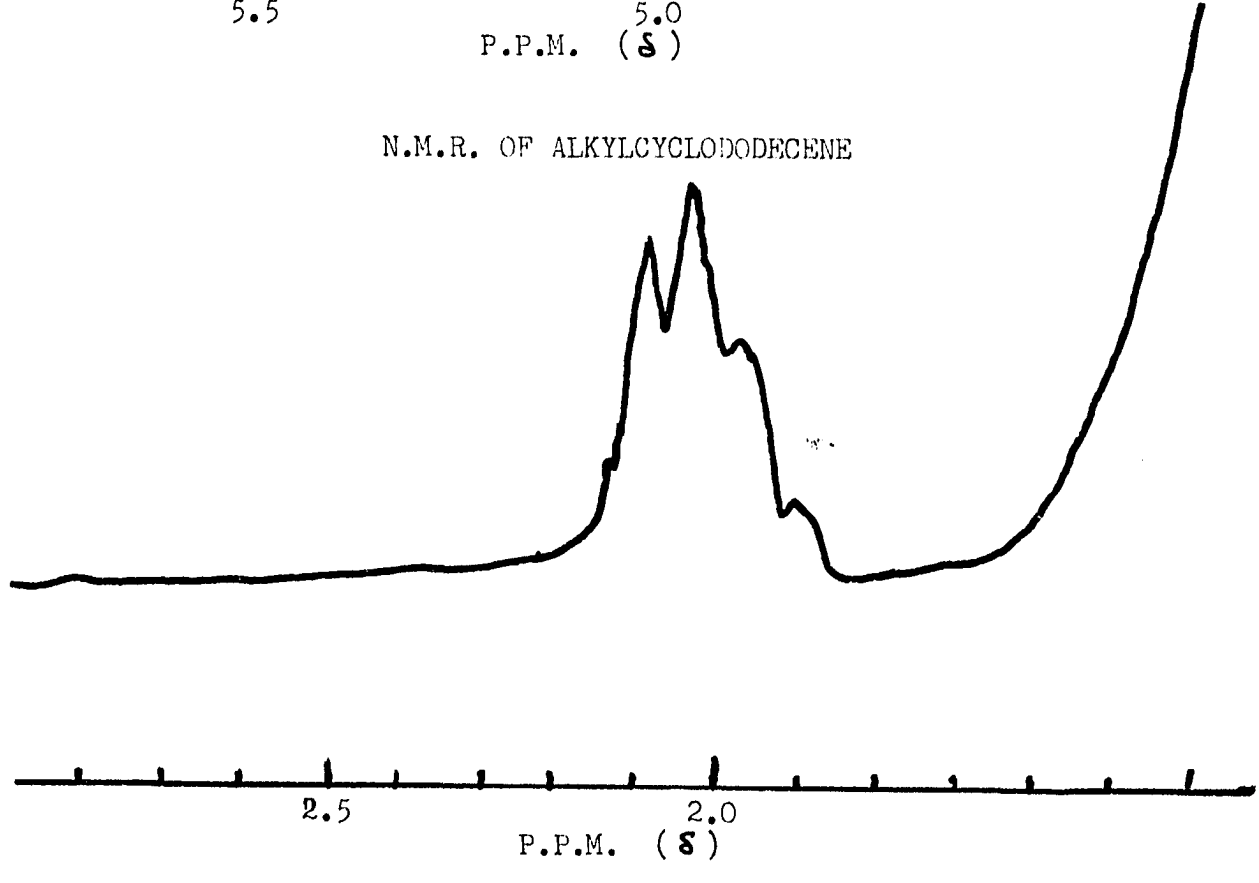

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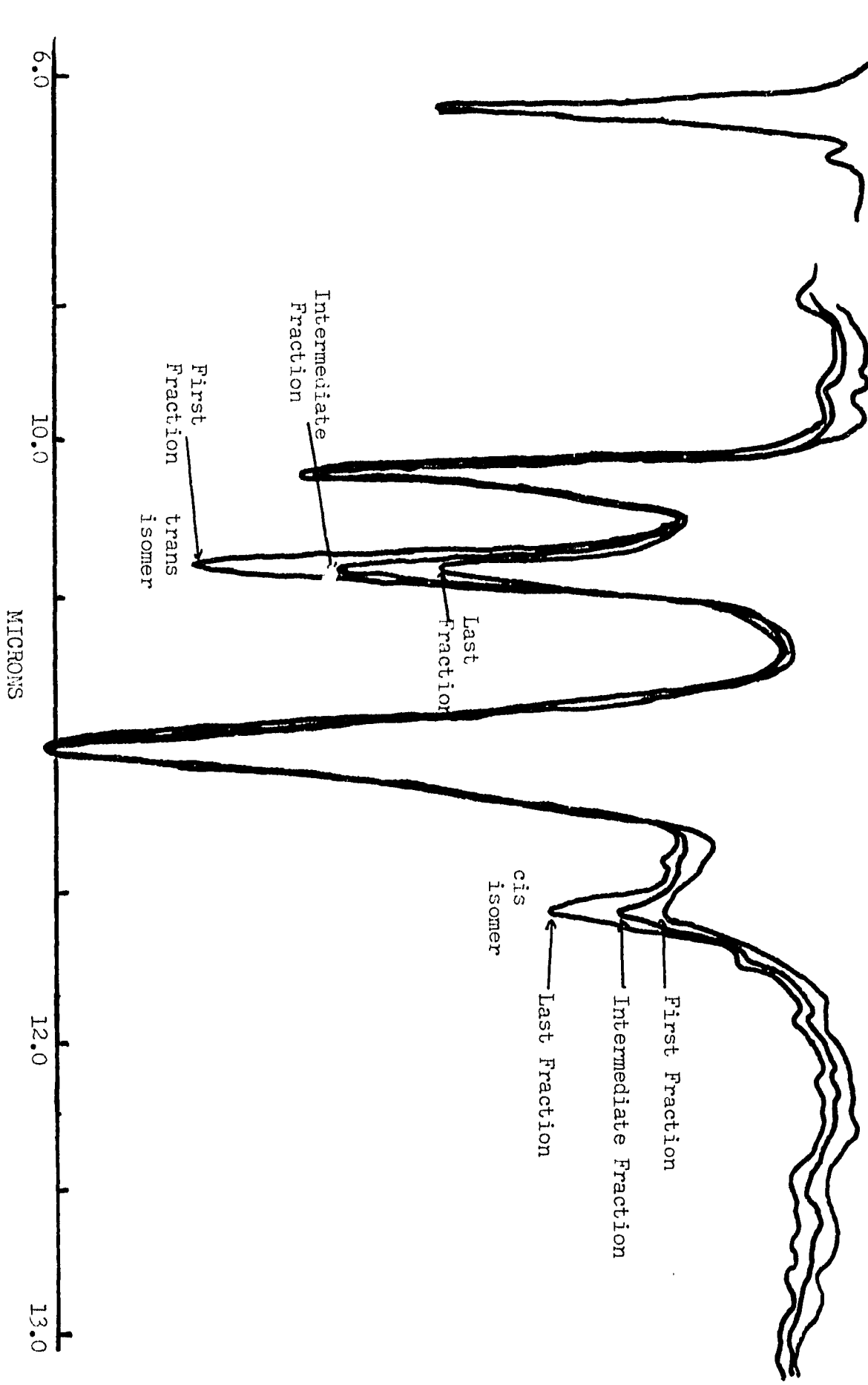

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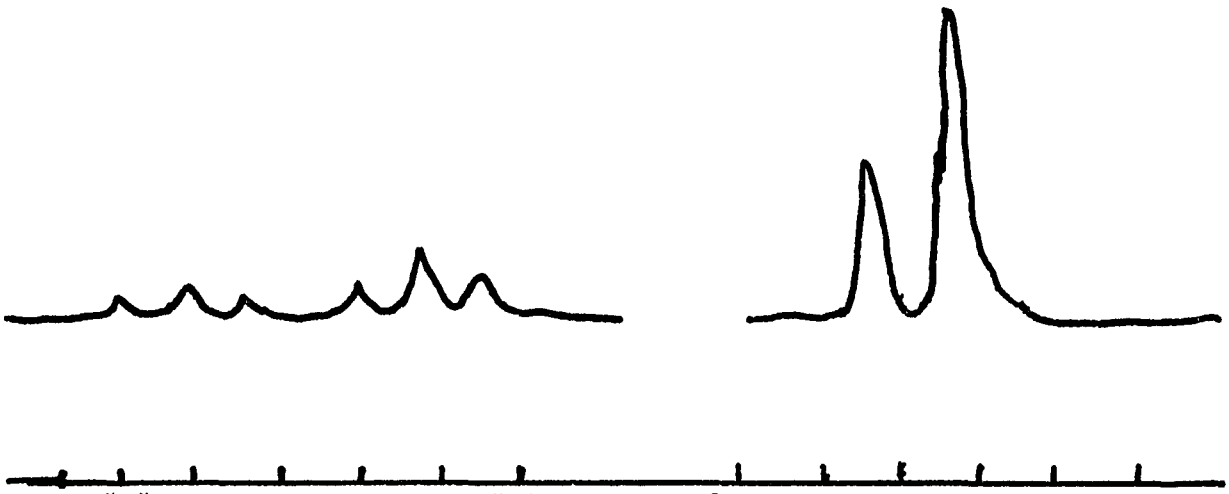

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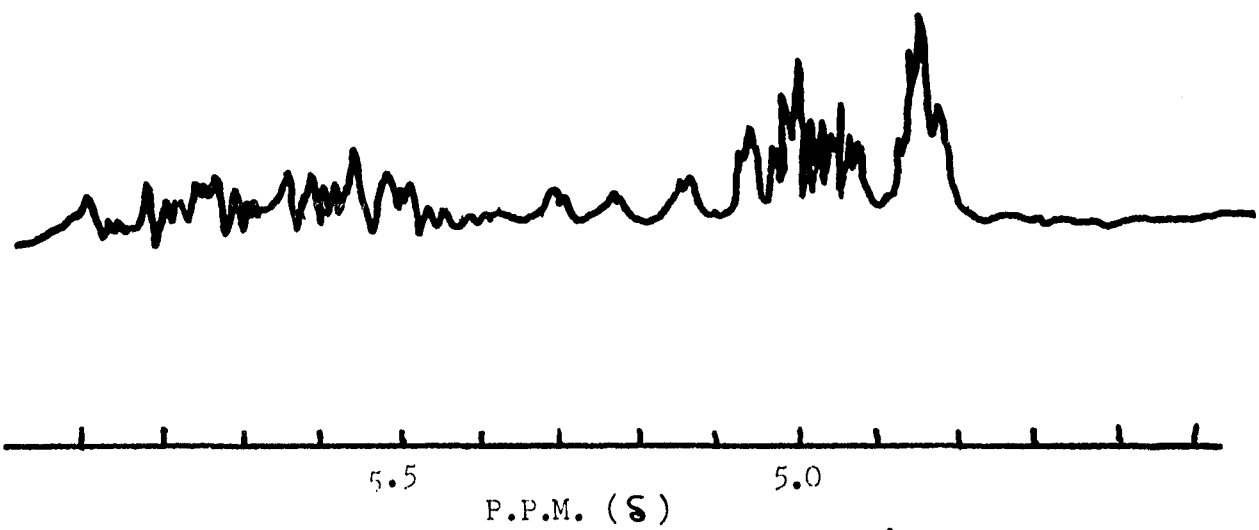

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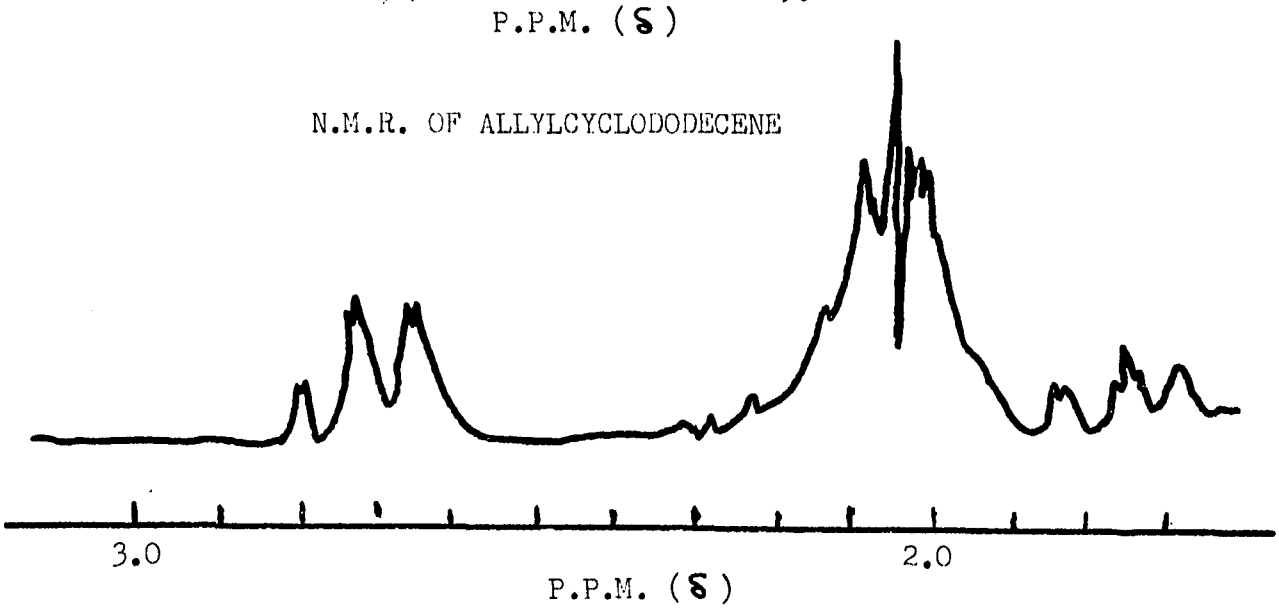

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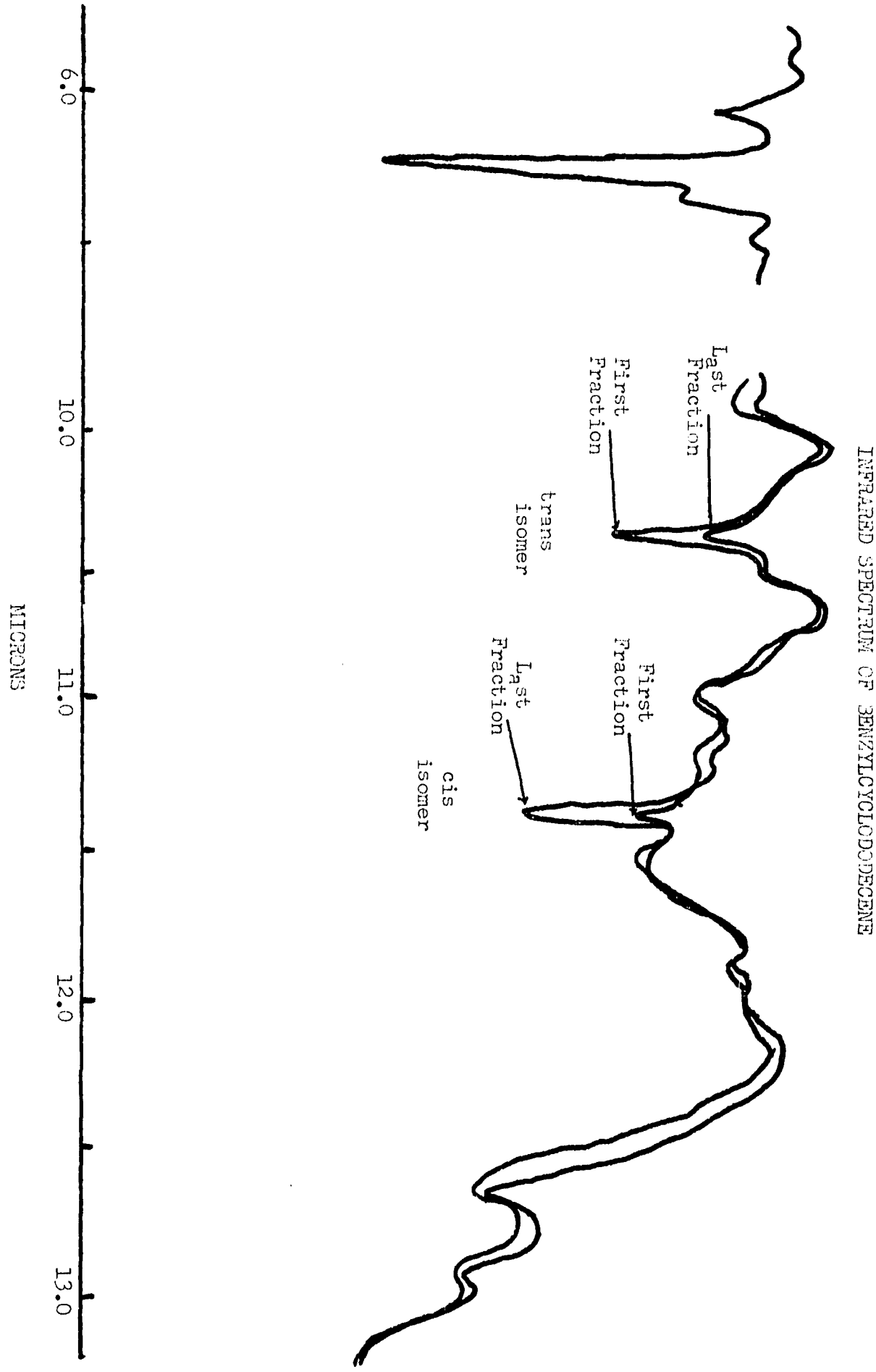

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VITA

Ronald Joseph Allain, the son of Mr. and Mrs. Edmond J. Allain, Jr. was born on May 15, 1940 in Baton Rouge, Louisiana. He attended Holy Family elementary school, and was graduated from Port Allen High School in 1958. In June of 1958, he entered Louisiana State University and was awarded the degree of Bachelor of Science in Chemistry and Physics in February, 1963. In February, 1963, he entered the Graduate School of Louisiana State University where he served as a teaching assistant.

He was married to Janet Carol Gaston on January 23, 1965, and is now the proud father of a son, Eric Joseph.

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EXAMINATION AND THESIS REPORT

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Major Field: Organic Chemistry

Title of Thesis: Part I. A New Synthesis of Dihydrojasmone
Part II. Dehydration Studies of Some Cycloalkanols

Approved:

C. R. McCallum
Major Professor and Chairman

R. D. Anderson
Dean of the Graduate School

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10/15/68